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Analysis of Volatile Products from the Slow Pyrolysis of Coal

North Carolina State Univ. at Raleigh

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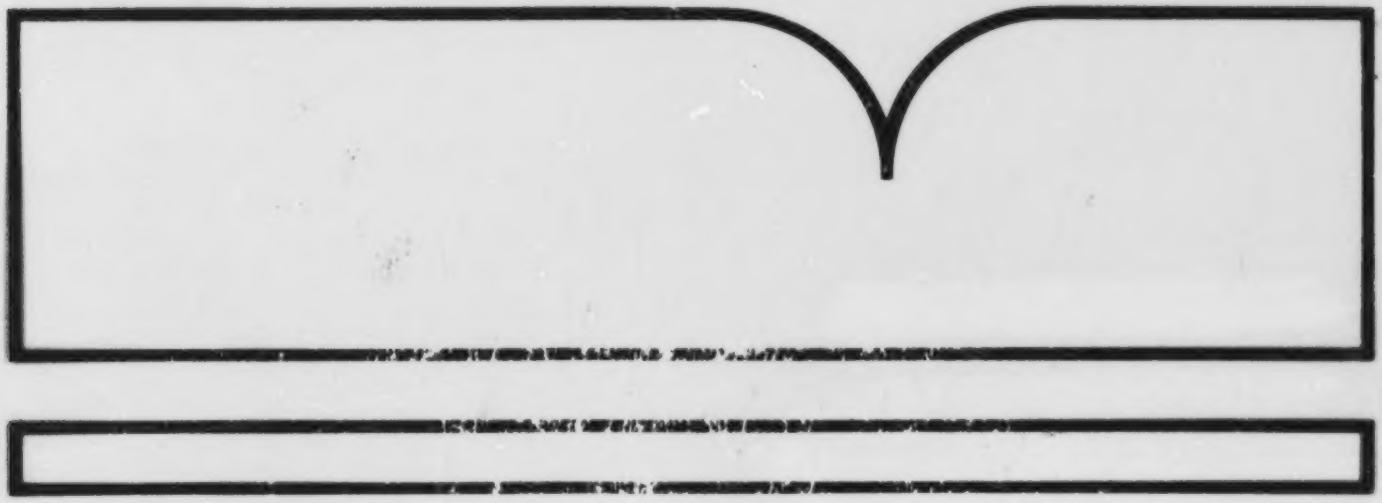

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ANALYSIS OF VOLATILE PRODUCTS FROM THE SLOW PYROLYSIS OF COAL

by

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16. ABSTRACT The report gives results of a study of the evolution of volatile matter from coals of various rank during fixed- and fluid-bed pyrolysis. The pyrolyses were performed at temperatures ranging from 400 to 1000 C and with heating rates ranging from 1.5 to 6.0 C/s. Effects of equilibrium temperature, heating rate, coal rank, and reactor design on weight loss, elemental volatilization, gas species production and product composition, and tar/gas production ratios were examined. Lignite, subbituminous, and bituminous coals exhibited the same weight loss versus temperature profiles at slow pyrolysis rates. Toluene, xylene, ethane, and total sulfur yields versus temperature varied from fixed- to fluid-bed conditions. All other compounds measured showed no such dependence on reactor design. For all systems studied, tar-to-gas ratios were lower (although overall weight losses were greater) for slow pyrolysis than for rapid pyrolysis. Tar yields increased and carbon oxide yields decreased with increasing coal rank.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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ABSTRACT

The evolution of volatile matter was studied for a subbituminous coal pyrolyzed in a bench scale fixed bed reactor, and for both a lignite and subbituminous coal pyrolyzed in a bench scale fluidized bed reactor. The pyrolyses were carried out under inert gas atmospheres, at a pressure of 135 kPa (5 psig), temperatures ranging from 400°C to 1000°C, and heating rates ranging from 1.45 to 6.0°C/s. The pyrolysis products -- tar, water, char, and gases -- were separated and analyzed. Primary gas, aliphatic hydrocarbon, aromatic hydrocarbon, and sulfur gas species were quantified by gas chromatography. The effects of equilibrium temperature, heating rate, coal rank, and reactor design on asymptotic weight loss, elemental volatilization, gas species production and product composition, and tar/gas production ratios were examined.

Plots of asymptotic (long-time) weight loss vs. temperature for the slow pyrolysis (<45°C/s) of the coals pyrolyzed in this study and three other coals ranging in rank from lignite to bituminous fall very close to a single curve over a temperature range of 400-1000°C. Similar plots based on published data for the rapid pyrolysis (10^3-10^5 °C/s) of three coals covering the same range in rank also fall close to a single curve, which lies below the slow pyrolysis curve and approaches it at temperatures of about 900°C.

Equilibrium weight loss and release of elemental oxygen, carbon, and hydrogen increased with temperature. In the fixed bed pyrolysis of subbituminous coal, the volatilization of sulfur and yields of hydrogen, carbon oxides, methane, benzene, thiophene, and carbon disulfide increased with temperature, while yields of toluene, xylene, C2-C4 aliphatic hydrocarbons, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan exhibited maxima at temperatures between 700 and 900°C.

In the fluidized bed pyrolysis of both lignite and subbituminous coal, yields of hydrogen, carbon monoxide, methane, ethylene, benzene, toluene, xylene, and thiophene increased with temperature, while volatilization of sulfur and yields of carbon dioxide, pyrolytic water, ethane, C3-C4 aliphatic hydrocarbons, hydrogen sulfide, carbonyl sulfide, methyl and ethyl mercaptans were maximized at temperatures between 700 and 900°C. The data on sulfur release suggest that the devolatilization of this element is affected at high temperatures by decreases in internal surface area and porosity of the coal particles.

Carbon disulfide was produced from the pyrolysis of subbituminous coal in both the fluidized bed and fixed bed reactors at temperatures greater than 800°C. It was not produced in the fluidized bed pyrolysis of lignite. Conversely, ethyl mercaptan was produced in the fluidized bed pyrolysis of lignite but did not appear in the products of either the fixed bed or fluidized bed pyrolysis of subbituminous coal. Yields of ethyl mercaptan were lower than yields of methyl mercaptan.

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For all systems studied, tar-to-gas production ratios dropped with increasing temperature. For slow pyrolysis over the temperature range of 400 to 900°C, tar production and tar-to-gas ratios were lower and weight losses greater than for rapid pyrolysis. As noted above, coal rank had no significant effect on asymptotic devolatilization. Tar yield increased and carbon monoxide, carbon dioxide, and pyrolytic water yields decreased with coal rank. The yields of the individual aliphatic hydrocarbons in the fluidized bed were greater for subbituminous coal than for lignite.

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INTRODUCTION

The principal obstacle to the use of coal as an energy source is environmental. Large quantities of potentially hazardous organic and inorganic species are formed during coal conversion operations, and must be captured and removed somewhere between the point of formation and the point of release of effluents to the atmosphere. If coal conversion operations are to be designed to be environmentally sound, the chemistry -- thermodynamics and kinetics -- of the formation of pollutants must be understood.

The first step in any coal conversion process -- combustion, gasification, or liquefaction -- is pyrolysis. The coal fed to the process is brought to a high temperature, leading to the formation and release of volatile species, including hydrocarbon, sulfur, and nitrogen gases, tars, and volatile trace metals. While much attention has been given in the literature to the principal reactions of pyrolysis, little has been done regarding the formation of minor but potentially hazardous species.

In the present study, several coals were pyrolyzed in laboratory-scale fixed and fluidized bed reactors, and the volatile products were quantitatively analyzed. The extents of total devolatilization, elemental release, and individual product species formation were correlated with the pyrolysis temperature, the heating rate, and the rank of the feed coal. This report describes the experimental systems used, presents the results obtained, and discusses the implications with respect to coal conversion processes. Information and results beyond those given in the report can be found in the dissertation of Gilman(1983).

BACKGROUND

Phenomenology of Coal Pyrolysis

Coal is composed of an inorganic phase (ash) and an organic phase. The ash consists of the pyrite, calcite, quartz, and other similar oxides and sulfides of metals which are uniformly distributed in the coal. The coal rank is determined by the nature of the organic phase. Aromaticity, the fraction of carbon found in aromatic structures, increases with rank. For subbituminous coals the aromaticity can be as low as 40% (Agreda et al., 1979). The remainder of the carbon is found in aliphatic chains and polycyclic aliphatic rings. At the other end of the spectrum, 100% aromaticity, is the fully condensed graphitic structure.

Coal rank is not a constant because coal is always in transition. This transition is labeled the process of coalification. It includes the following stages:

1) Deposit of organic matter
2) Peat
3) Lignite
4) Subbituminous
5) Bituminous
6) Anthracite
7) Pure Carbon, Graphite

Pyrolysis is an artificial means of accelerating the coalification process. Application of heat causes the decomposition of the feedstock, producing a solid residue, char, as well as tar, water, and pyrolytic gases, the latter being termed volatiles or volatile matter. The volatiles consist of a mixture of carbon dioxide, water vapor, and combustible gases. The combustible gases are carbon monoxide, hydrogen, aliphatic and aromatic hydrocarbons, and sulfur gases.

Howard (1963) has discussed the order of appearance of volatile species when coal is heated at a constant rate. Following the release of moisture from the parent coal, the sequence is chemical water, carbon dioxide, carbon monoxide, higher hydrocarbons (tars, etc.), ethane, methane and finally hydrogen. The weight lost by the parent coal and the resulting composition of the volatiles depend on the time/temperature history of the pyrolysis.

The factors that influence the time/temperature history are the rate of temperature rise, the final temperature attained, and the duration of decomposition at that temperature. When the decomposition products are rapidly removed and diluted in the gas phase, chemical interactions are less likely to occur, reducing the possibilities for

recombinations of reactive constituents.

Salcewicz et al.(1967) proposed that coal pyrolysis occurs in four stages: 100°-300°C, 300°-500°C, 500°-700°C, and >700°C:

1. The initial stage, which precedes the carbonization proper, is characterized by the loss of water by the coal. In this stage, a certain loosening of the structure of the coal substance may occur under the influence of the energy absorbed by the coal as a result of the temperature increase.

2. In the second stage, from 350 to 500°C, physicochemical changes and chemical reactions accompanying plasticization take place. The volatiles are evolved from a semiliquid and sometimes liquid substance which, by going through successive plasticization changes, undergoes not only a physical but also a chemical modification. An intensive detachment of side chains and radicals takes place, and the solidifying coal substance loses more hydrogen and oxygen than carbon in weight.

3. In the third stage, from 500 to 700°C, the volatiles are evolved from solidified semicoke. The process of polymerization and condensation of the coal substance begins, the volatiles show an increasing amount of products of these reactions, namely, carbon monoxide and carbon dioxide and methane type light hydrocarbons.

4. The fourth stage, above 700°C, shows the weight of the volatiles evolved to be insignificant and that the volatiles are composed of hydrogen and methane. The evolution of hydrogen and oxygen and the increase of the coal content undergo a marked inhibition, and the coalification index increases very abruptly, asymptotically approaching the limiting value, i.e., infinity.

Devolatilization of a bituminous coal and a lignite have been performed by Suuberg et al.(1979), who concluded that thermal decomposition occurs in several overlapping phases, each of which is dominated by a single product or class of products. Four such regimes for the bituminous coal have been described:

1. Low temperature (100°C) removal of moisture.

2. Liberation of pyrolytic water, or water evolved beyond the amount attributable to moisture as measured by the ASTM

techniques, at temperatures below 400°C.

3. A broad phase occurring between 400 and 900°C, during which the coal softens and hydrocarbons are evolved.

4. A phase occurring above 900°C in which CO and H_2 are the principal products.

In comparison, the pyrolysis of lignite was said to occur in five phases:

1. The low temperature removal of moisture.

2. Low temperature carbon dioxide and hydrocarbon evolution (about 450 - 600°C).

3. Evolution of pyrolytic water (600 to 700°C).

4. Evolution of hydrocarbons, hydrogen, and carbon oxides (700 - 900°C).

5. Evolution of carbon oxides (greater than 1000°C).

The cited temperature intervals were observed in experiments using a heating rate of 1000°C/s. For lower heating rates, the limits as well as the widths of the temperature intervals decrease.

Analyses of pyrolysis products show that the product structures are similar to the structure of the feedstock (Howard, 1963). The IR spectra of vacuum pyrolysis coal tars were found to be similar in character to those of the parent coal (Solomon, 1981). Figure 1 illustrates Solomon's schematic presentation of coal pyrolysis in which a hypothetical coal molecule is cracked by pyrolysis yielding initial fragments similar to the parent molecule (Haggin,1982).

Campbell (1976) has discussed the production of primary gas species and light hydrocarbons from parent coal functional groups. Hydrogen gas evolves from the fusion of aromatic ring structures (lamellae) in the coal matrix. This reaction can be schematically represented as

$$Ar\text{-}H + Ar'\text{-}H \longrightarrow Ar'\text{-}Ar + H_2$$

where Ar and Ar' represent particular lamellae structures. As the pyrolysis temperature is raised there is further fusion of the lamellae and the production of hydrogen increases.

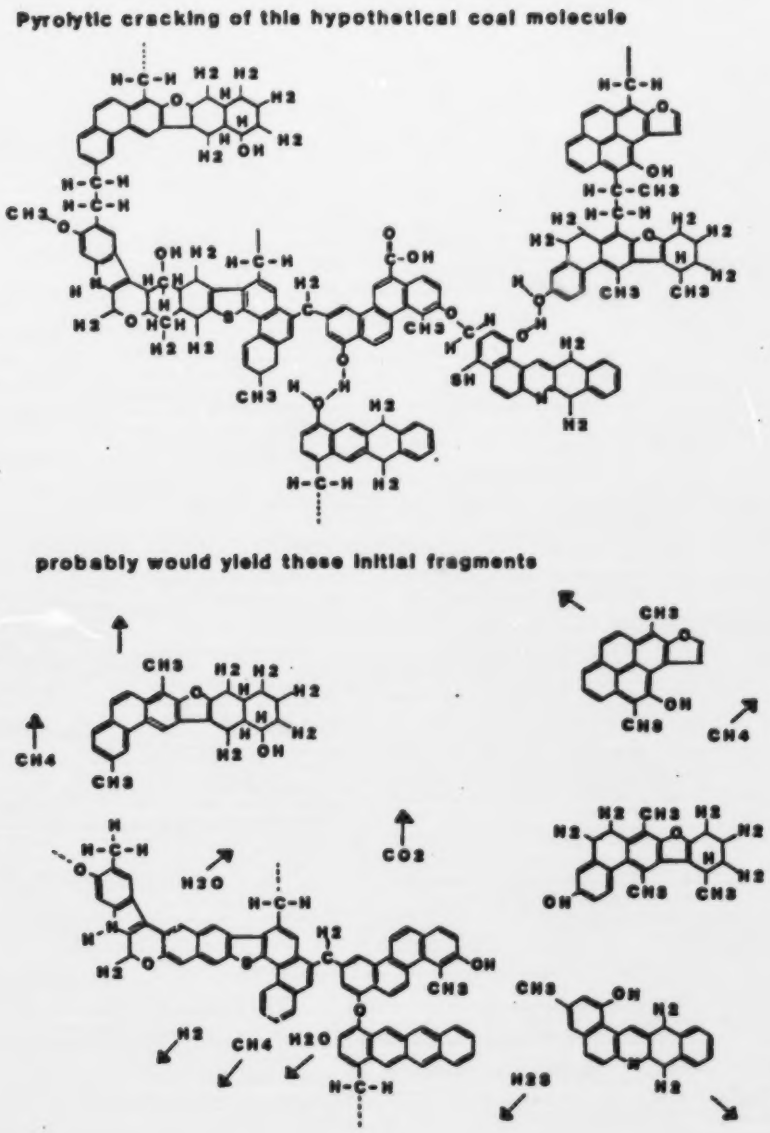

FIGURE 1 SCHEMATIC OF COAL PYROLYSIS MECHANISM

The formation of carbon dioxide is attributed by Campbell to the decomposition of carboxylic acid functionalities at temperatures of 500°C and to carbonate decomposition in the mineral matter at temperatures of 650 to 700°C. Above 850°C there is no further production of carbon dioxide. The production of carbon monoxide has been attributed to several functionalities in the feed coal, primarily ether linkages, ketone groups, and heterocyclics. At temperatures less than 500°C CO arises from the decomposition of ether links and carbonyl groups, and at temperatures greater than 500°C it is produced from the degradation of heterocyclic compounds (Fitzgerald, 1959). Some of the carbon monoxide in the product gas of high temperature pyrolysis may be the result of carbon dioxide contacting char carbon.

Methane and other light hydrocarbons are produced at temperatures in the vicinity of 500°C as the result of dealkylation, in which aliphatic side chains and inter-lamelle linkages are cracked (Campbell, 1976). The fracture of the aliphatic side chains from the aromatic matrix has been investigated by Depp et al.(1956). The methylene and ethane linkages which form bridges between aromatic rings are quite weak. At temperatures greater than 550°C, methane is produced from dealkylation and char autohydrogenation reactions (Fitzgerald and van Krevelen, 1959).

The production of volatile sulfur species has been discussed by Attar (1978). The distribution of sulfur in the pyrolysis products depends on how the sulfur is distributed between the organic and inorganic phases of the coal feedstock.

Variables Affecting Pyrolysis Rates and Equilibria

The basic parameters affecting the coal pyrolysis process are coal rank, pyrolysis temperature, heating rate, duration of heating, particle diameter, reactor design, reactor pressure, and for fixed bed reactors, bed depth.

Heating rates have been divided into two categories, slow to intermediate and fast. When coal is heated at a slow to intermediate rate (<100°C/s), the time required for complete devolatilization of the coal is significantly less than the time required for heating the coal particles to the final temperatures (Wen and Lee, 1979). Rapid pyrolysis or flash pyrolysis is attained by imposing heating rates greater than 1000°C/s. Electrical devices with resistor-controlled heating circuits can achieve heating rates as high as 100,000°C/s. For rapid pyrolysis the duration of heating is usually less than 30 seconds in order to avoid overheating of the electrical resistors (Anthony and Howard, 1976).

In a review of fast pyrolysis, Horton (1979) proposes that a quasi-equilibrium is reached before the coal particles are quenched. The pyrolysis process appears complete but additional devolatilization occurs when the quenched char particles are reheated in a fixed bed reactor. This implies that if the coal particles had been maintained at the elevated temperature for a longer period of time in the fast pyrolysis reactor (wire screen or laminar flow reactor), additional pyrolysis would have occurred.

Heat and mass transfer are limited by particle diameter. Generalizations concerning particle size effects have been compiled by Anthony and Howard (1976).

1. If the dominant heat transfer resistance lies between the coal particle and its environment, the particle temperature is uniform during heating and the rate of temperature rise decreases with increasing particle size.

2. Pyrolysis rates during heating increase with decreasing particle size.

3. The reaction during the heating process becomes more negligible as the heating rate is increased beyond some critical heating rate.

The transition between kinetic and heat transfer control occurs at a particle size below which the center temperature approaches the surface temperature before significant reaction can occur. For coal particles with diameters smaller than 100um the pyrolysis rate is kinetically controlled and depends on the final pyrolysis temperature, and not the heating rate or particle size. For larger coal particles the external heat transfer coefficient can be large enough to produce significant temperature gradients within the particle. The particle size at which the devolatilization shifts from being kinetically controlled to being heat transfer controlled has been predicted by Koch et al. (1969) to be related to heating rate as shown below.

Heating Rate $^{o}C/s$	100	1,000	10,000
Critical Diameter um	2,000	500	200

Devolatilization of larger coal particles (295 to 4,760um) has been modeled in terms of a shrinking spherical liquid core in a porous char matrix (Essenhigh, 1963). The rate of devolatilization is controlled by volatiles transport from the liquid surface through the char shell.

Pyrolysis Reactor Design

Three types of reactor designs have been used in most pyrolysis experiments. They are the fixed bed, electrified wire mesh, and the "free-fall" reactors.

In the fixed bed reactor coal particles are placed inside a porcelain boat or crucible in the heated section of the furnace. An inert gas sweeps past the porcelain boat or crucible, carrying the volatile prolysis products. Low heating rates and long residence times are obtained. The major drawbacks to this reactor design are the heating of the porcelain boat before the heating of the coal sample, the potential uneven heating of a fixed bed of layered coal particles, and readsorption of evolved material in the bed. These factors introduce unknown lagtime and a non-homogenous temperature profile across the fixed bed.

In the second experimental design powdered coal is placed on a wire screen or mesh. The mesh is attached to an electrical system which allows for the independent control of the heating rate and the final sample holding time and temperature. Heating rates from 10^2 to 10^4 $^oC/s$ can be attained. Caution should be used in the study of the volatiles composition from such apparatus because catalytic cracking on the hot screen can alter the volatiles distribution (Anthony and Howard, 1976).

The "free-fall" reactor design introduces coal particles into a preheated gas stream. The ambient atmosphere, final temperature, and the particle loading are controlled. The heating rate of the coal particles depends upon the particle environment and the mixing of the carrier and main stream gas flows.

A fourth reactor type -- namely, a bench-scale fluidized bed reactor -- has been utilized in the present study. A description of this reactor is proved in the Experimental Design section of this report.

Prediction of Volatiles Yield

Anthony and Howard (1976) report measurements of coal weight loss (volatiles yield) for Pittsburgh Seam bituminous coal as a function of residence time (0-20s), heating rate (65-10,000$^oC/s$), final temperature (400-1100^oC), total pressure (0.0001-7MPa), hydrogen partial pressure (0-7MPa), and particle size (70-1000um). The volatiles yield varies with the gas atmosphere. For a helium atmosphere the volatiles yield increases significantly with decreasing pressure and increasing final temperature but only slightly with increasing heating rates, and decreasing particle size. In a hydrogen atmosphere the effect of particle size on volatiles yield is substantial. At 7 MPa and 1000^oC, the reduction of the particle size from 1000 to 70 um increases the

volatiles yield from 44 to 59 % (as-received) of the original coal.

Mass Balances for Coal Pyrolysis

Suuberg et al.(1978, 1979) pyrolyzed lignite and bituminous coal in a batch reactor with electric circuitry which permitted independent control of the heating rate (10^2-10^4°C/s) and final sample holding time and temperature (150-1100°C for up to 30 s). The pyrolysis products were quantified and elemental compositions were determined. Mass and elemental balances for the lignite were obtained, and the products of the lignite pyrolysis were compared to those from the pyrolysis of the bituminous coal.

Modeling of Coal Pyrolysis

Van Heek and Juntgen (1968) proposed that modeling attempts should focus on the individual volatile species. The implication was that each volatile species was formed by a specific reaction within the coal matrix, with each reaction characterized by a different activation energy.

Kobayashi (1972) used a model of two competing first-order reactions to correlate devolatilization data published by Badzioch and Hawksley (1970). This approach offered an explanation of the effects of temperature and heating rate on devolatilization. Anthony and Howard (1976) describe a model which presumes that thermal decomposition of a coal molecule of a large number of independent chemical reactions. Their model includes a first-order devolatilization equation with a Gaussian Distribution of activation energies.

A first-order non-isothermal model was developed by Agreda et al.(1979, 1980) to correlate devolatilization data for three coals -- Montana Rosebud Subbituminous, New Mexico North Barber No. 8 Subbituminous, and Montana Beulah Zap Lignite -- in a laminar flow reactor. Using the same reactor, Felder et al. (1982) found that Kobayashi's two-parallel-reaction model provided the best correlation of the devolatilization data for subbituminous coal and Anthony's distributed activation energy model was found best for bituminous coal.

A relationship between a coal's organic structure and the products of its thermal decomposition has been proposed by Solomon (1979) for the devolatilization of bituminous coal and lignite. The evolution of each product is characterized by first order rate constants, presented in Table 1, which do not vary with coal rank. The differences between product distributions for different coals are due to differences in the concentrations of functional groups in the coals.

Table 1

Solomon's Kinetic Constants for Lignite and Bituminous Coals

Functional Group	Kinetic Rates
carboxyl	$k_1 = 6 \exp(-4000/T) \text{sec}^{-1}$
hydroxyl	$k_2 = 30 \exp(-4950/T)$
ether loose	$k_3 = 7000 \exp(-10300/T)$
ether tight	$k_4 = 400 \exp(-12000/T)$
nitrogen loose	$k_5 = 200 \exp(-7699/T)$
nitrogen tight	$k_6 = 290 \exp(-12700/T)$
aliphatic	$k_7 = 750 \exp(-8000/T)$
aromatic H	$k_8 = 3600 \exp(-12700/T)$
non-volatile C	$k_9 = 0$
tar	$k_x = 750 \exp(-8000/T)$

The functional group kinetic approach was also adopted by Gavalas et al.(1981), who modeled coal as a collection of 14 functional groups including aromatic rings, aliphatic chains and bridges, and oxygen-carrying groups. The functional group concentrations vary with the type and origin of the coal. The chemical changes taking place during pyrolysis are a set of free radical reactions undergone by the different groups, at rates which can be determined from model compound studies.

EXPERIMENTAL DESIGN

Research was performed using bench scale batch fixed bed and fluidized bed reactors. The coal feed to both reactors was set at 5 grams, which provided adequate samples of the pyrolysis products for analysis.

Fixed Bed Reactor

The fixed bed reactor, shown in Figure 2, was constructed using a design of Agreda et al.(1979). The char from the pyrolysis of the coal is collected in the porcelain boat which originally held the feed coal. Modifications were made to collect evolved tar and water using 0.5 gram of quartz wool in the extreme downstream portion of the quartz tube. An evacuated 1.0 liter stainless steel bomb is placed downstream of the quartz wool for the collection of the pyrolysis gases.

The heating element of the system includes a Lindberg Model 54032 single zone tube furnace and a Lindberg Model 59344 digital control console. The heating zone of the furnace is twelve inches long. The reactor temperature of the furnace is measured with an Omega Model 2160A digital thermocouple with a 316 SS sheath. The temperature in the reactor can be varied between 200 and 1200^{o}C. A quartz tube of 26 inches in length and one inch in diameter is used as the reactor. Pulverized coal samples weighing approximately five grams are placed in glazed porcelain boats and are introduced into the reactor.

A 1/16-inch outer diameter stainless steel slide wire is used to insert the pyrolysis boats into the furnace. The slide wire holder is sealed with an O-ring. Quartz wool is packed at the extreme downstream portion of the pyrolysis tube to collect some of the volatile tar. The noncondensing volatiles pass through valve V4 and are collected in an evacuated one liter stainless steel bomb. Before and after a run the gas is sent through a stainless steel 10 psig one way valve (V-5) and into a scrubber bottle containing 70 ml of 10N sodium hydroxide solution. All connections are made with Swagelock^{R} connectors and fittings.

(Note: just using quartz wool at the tube outlet led to undercollection of condensable species, and incomplete closure of mass balances in runs made with this reactor. Improvements could have been achieved by using a packed cold trap, but before this was done it was determined that the fluidized bed to be described provided much more reliable data, and so the modifications to the fixed bed were not made.)

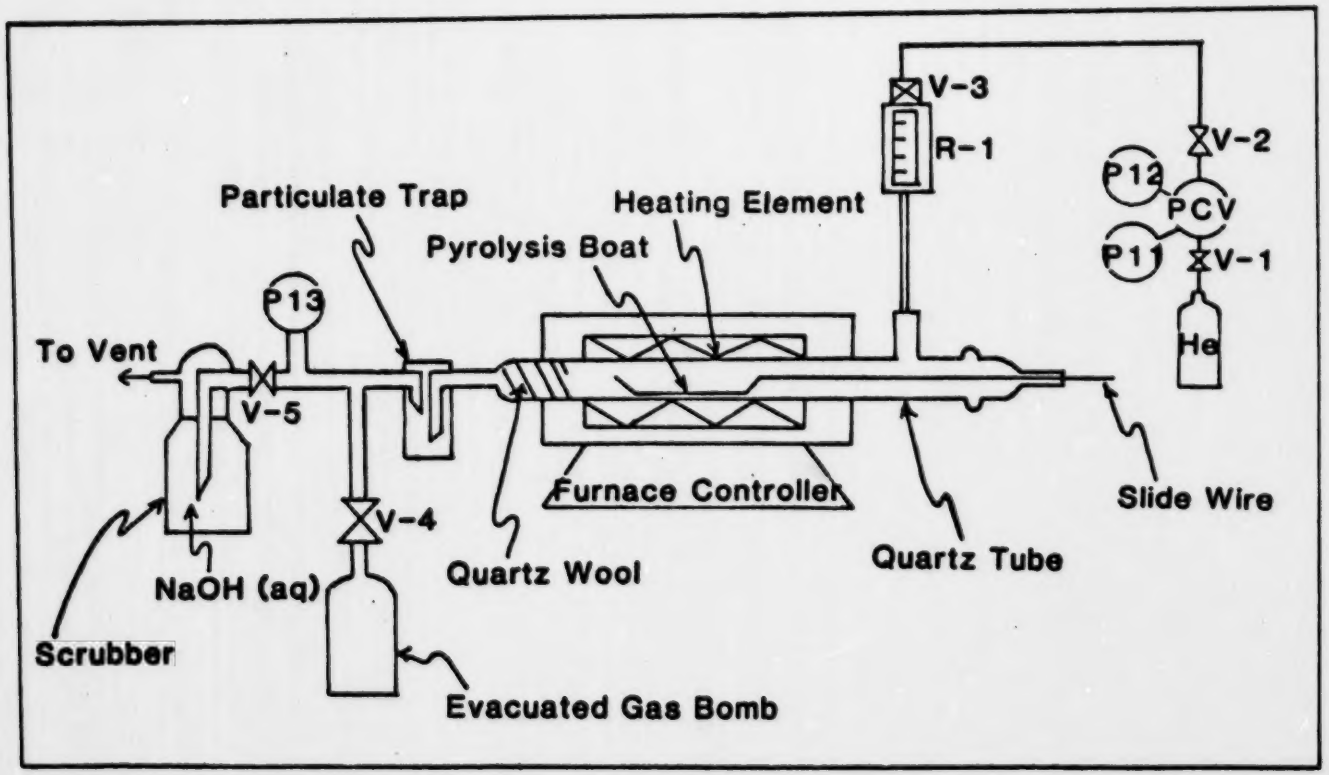

FIGURE 2 FIXED BED REACTOR SYSTEM

The temperature inside the furnace is determined by inserting the 1/16-inch thermocouple instead of the slide wire. The temperature controller feedback loop utilizes a Platinel II thermocouple embedded in the heating element's ceramic support. Therefore, it is necessary to correlate the controller readings with the actual reaction zone temperature. Previous work (Agreda et al., 1979) has shown that the peak temperature occurs at the center of the furnace and the temperature profile is fairly flat in a 3-inch section at the center of the furnace. The porcelain pyrolysis boats are placed in this zone for the runs.

Helium and argon are used as sweep gases. The gas supply consists of an A size cylinder fitted with a regulator (PCV). The cylinder is opened by valve V1. Cylinder pressure is measured by a high pressure gauge (P11). The downstream pressure is measured by a low pressure gauge (P12). The flow rate of the sweep gas is regulated by valves V2 and V3. Flow to the pyrolysis tube is metered with a calibrated Air Products rotameter, and set at 0.2 SCFM.

There are three controlled variables in the fixed bed system: the furnace temperature, the pre-heated sweep gas flow rate, and the residence time of the coal in the furnace. The coal heating rate is a function of the furnace temperature and the heat capacity of the coal and the porcelain boat.

Heat is transferred from the heating elements of the Lindberg furnace by conduction through the quartz tube and through the bottom and sides of the porcelain boat, and by radiation from the quartz tube above the porcelain boat. The temperature-time history is constructed assuming that the heating and cooling rates of the coal are approximated by those of spent char. To determine these rates, a porcelain boat was filled with spent char with a 1/16 inch grounded chromel-alumel thermocouple placed in the middle of bed. The porcelain boat, the spent char, and the thermocouple were introduced into the reaction zone of the furnace. The temperature rise was monitored as a function of time. The heating curves are shown in Figure 3.

It takes approximately 200 seconds to heat the reactor zone to the desired equilibrium temperature (T_f). This temperature is maintained for 400 seconds. The average heating rate is estimated by a linear approximation:

$$m = \frac{T_f - T_o}{t_h}$$

where T_f = equilibrium temperature
T_o = initial temperature
t_h = time for heating to T_f

Using this equation, the heating rates are found to range from 1.45°C/sec at 500°C to 6.0°C/sec at 1100°C.

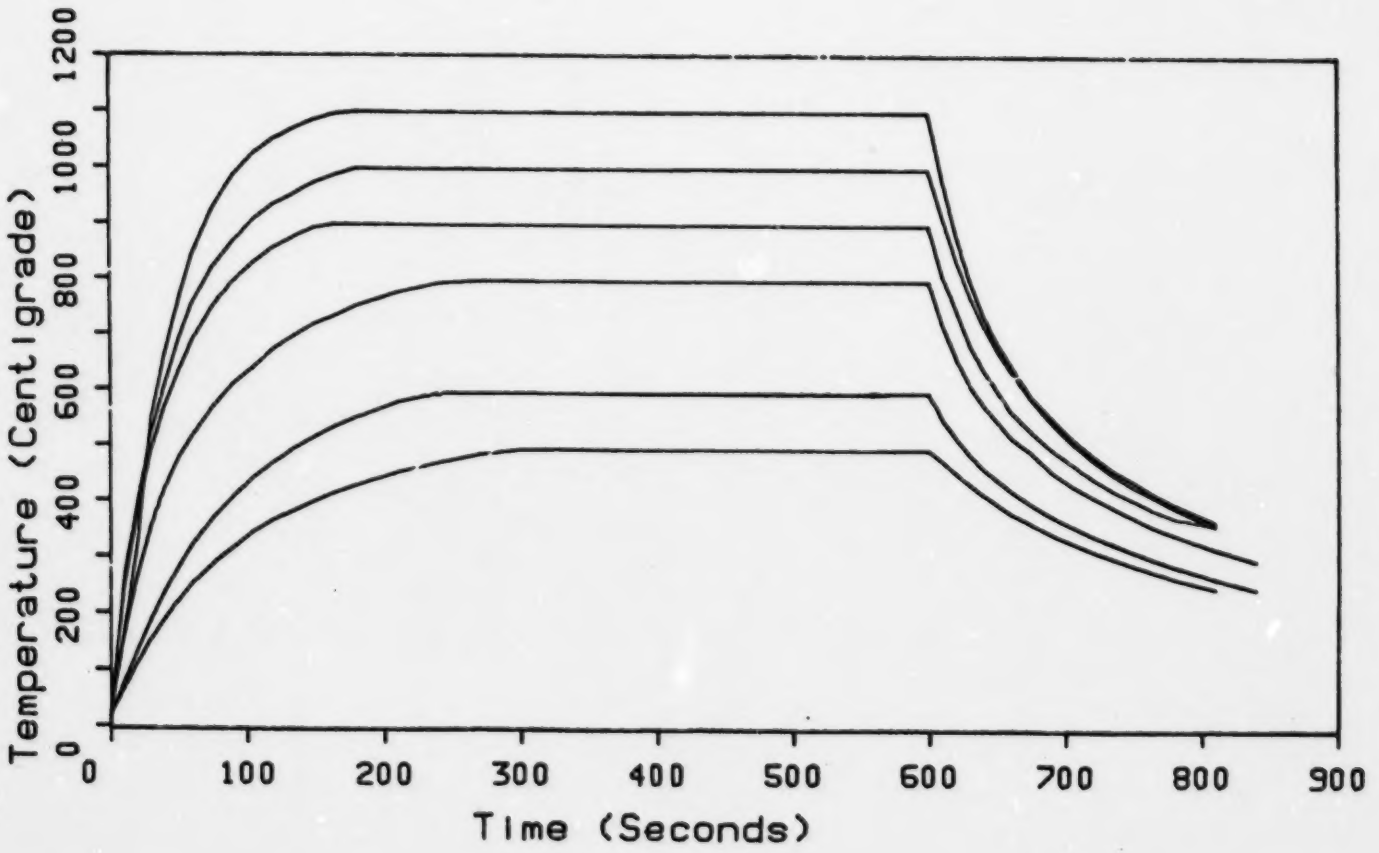

FIGURE 3. HEATING RATE CURVES FOR THE FIXED BED

The experimental procedure for operating the fixed bed reactor is as follows:

1. Weigh out two 0.5 gram samples of quartz wool. Pack one of the samples of quartz wool in the extreme downstream portion of the quartz reactor tube.

2. Set the digital controller from the temperature calibration curve.

3. Turn on sweep gas. Set gas flow rate at 0.2 SCFM.

4. Monitor reactor peak temperature and wait until digital temperature readout is at the desired level for at least 30 minutes. (Usually at least 3 hours are needed for reactor temperature to equilibrate.)

5. Replace thermocouple with slide wire.

6. Weigh 5.0 gram samples of coal in the pre-weighed porcelain boat.

7. Place boat in mouth of the quartz tube. Connect slide wire to the boat's hook.

8. Close tube and seal gas-tight with the Swagelock fitting and the O-ring.

9. Purge with sweep gas for at least 5 minutes. The purpose of this step is to ensure that no air remains in the system, hence combustion cannot occur. Check reactor pressure using gauge P13.

10. Push the boat with the slide wire into the center of the reaction zone.

11. Keep boat in the reactor zone until pyrolysis is completed.

12. Collect the gases in the evacuated bomb.

13. Pull boat out of the reaction zone.

14. Allow the pyrolysis boat to cool for 5 minutes before opening the tube to ensure that the pyrolyzed coal does not combust.

15. Open mouth of the pyrolysis tube and remove boat.

16. Place boat in desiccator. Wait until it cools completely (at least 15 minutes).

17. Weigh the boat and the char. Determine the weight of the char.

18. Remove the quartz tube from the furnace and allow it to cool to room temperature. Remove the quartz wool from the pyrolysis tube. Weigh the quartz wool, now laden with tar and water. Determine the weight of the tar and water.

19. Turn off the power. Cut off the gas flow.

20. Label and store quartz wool in desiccator. Subsequently dry and reweigh to determine relative amounts of tar and water.

Fluidized Bed Reactor

The fluidized bed reactor, Figure 4, was developed by modifying the fixed bed reactor design. A stainless steel tube (5/8 in. I.D.) with top and bottom stainless steel frits contains the 5 grams of pulverized coal. Water and tar capture were improved by adding a cold trap downstream from the reactor zone. The cold trap includes a 125 ml Erlenmeyer flask containing 0.5 gram of quartz wool. The flask is immersed in an ice bath to condense the the tar and water from the volatiles. The tubing from the fluidized bed to the cold trap is wrapped with a heating tape so that the tar and water will not condense prior to entering the trap.

There are two heating units for the fluidized bed. A Lindberg Model 55035 furnace functions as a gas preheater, heating the sweep gas from room temperature to 300^{o}C. The heating element for the fluidized bed includes a Lindberg Model 54032 single zone tube furnace and a Lindberg Model 59344 digital control console. The heating zone of the furnace is twelve inches long. The reactor temperature can be varied between 200 and 1200^{o}C.

The temperature inside the fluidized bed is monitored by a 1/16-inch diameter chromel-alumel thermocouple placed in the fluidized bed through an opening in the top frit. Initially, runs using spent char were performed to ensure the fluidization of the bed at selected temperatures. By raising and lowering the thermocouple in the bed, temperature changes in the vertical direction were monitored. The gas flow functions to maintain a fluidized particle bed and to remove the volatile products of the pyrolysis.

Helium and argon are used as sweep gases. The results obtained have not shown any noticeable dependence on which gas was used. The gas supply consists of an A size cylinder fitted with a regulator (PCV). The cylinder is opened by valve V1. Cylinder pressure is measured by a high pressure gauge (P11). The downstream pressure is measured by a low pressure gauge (P12). The downstream flowrate is regulated by valves V2 and V3. Flow to the preheater is metered with a calibrated Air Products rotameter (R-1). A 150 watt Fisher heating tape is used to heat trace the gas line exiting the preheater. Another heating tape traces the

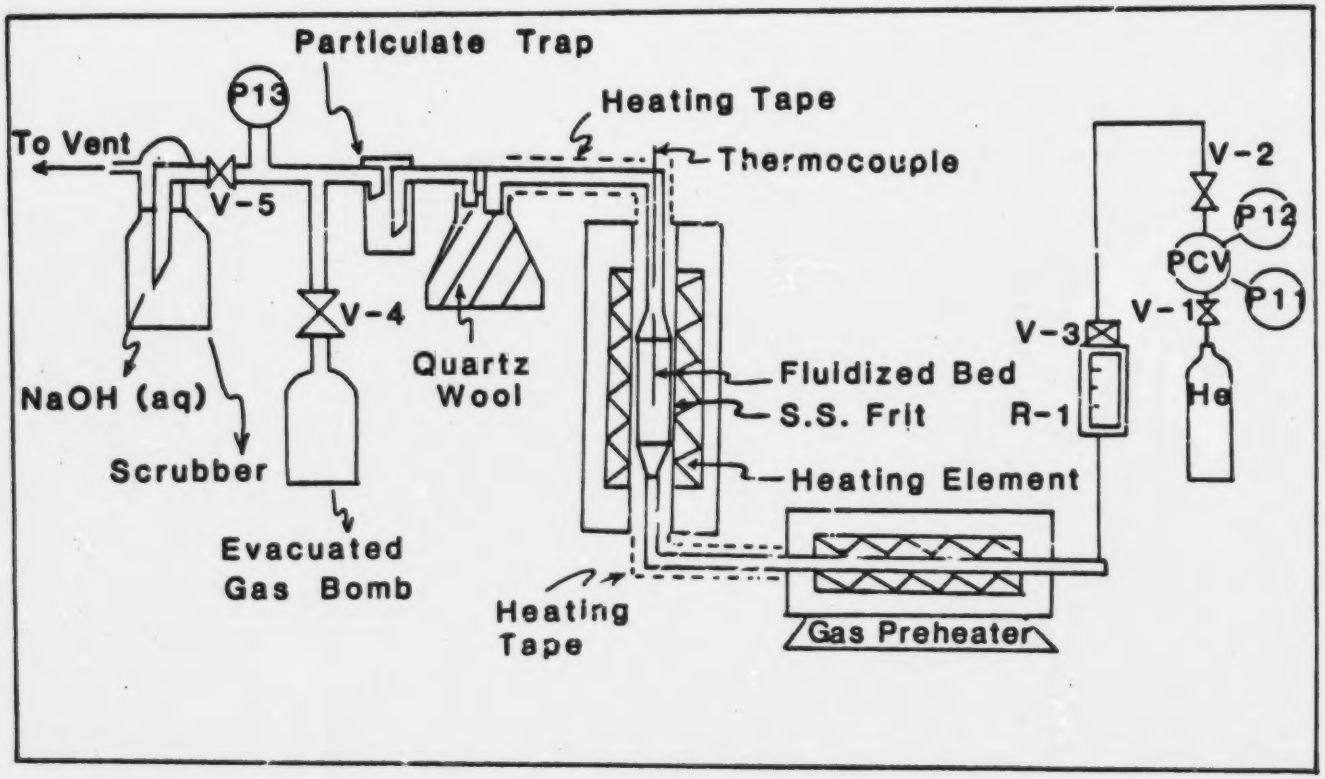

FIGURE 4 FLUIDIZED BED REACTOR SYSTEM

line from the reactor furnace to the cold trap.

Quartz wool is packed in the Erlenmeyer flask of the cold trap to collect the tar and water. The noncondensing volatiles pass through valve V4 and are collected in an evacuated one-liter stainless steel bomb, or a glass bomb coated internally with hexamethyldisilizane to reduce the adsorption of hydrocarbons and sulfur gases. Before and after a run the helium is sent through a stainless steel 10 psig one way valve (V-5) and into a scrubber bottle containing 70 ml of 10N sodium hydroxide solution. All connections were made with Swagelock® connectors and fittings.

The temperature-time history of the bed was constructed assuming that the heating rates of the coal are approximated by those of spent char. The stainless steel tube was filled with spent char with a 1/16 inch grounded chromel-alumel thermocouple placed in the middle of the bed, and was introduced into the reaction zone of the furnace. The temperature rise was monitored as a function of time. The heating curves are shown in Figure 5.

It takes from 200 to 300 seconds to heat the fluidized bed to the desired equilibrium temperature (T_f). This temperature is maintained for approximately 600 seconds. The average heating rate in the fluidized bed is estimated by a linear approximation:

$$m = \frac{T_f - T_o}{t_h}$$

where T_f = equilibrium temperature
T_o = initial temperature
t_h = time for heating to T_f

Using this equation, heating rates were found to range from 2.22°C/sec at 400°C to 2.38°C/sec at 1000°C.

The minimum fluidization velocities for the fluidized bed at 400°C and 1000°C are 1.47 and 0.99 feet/second, respectively. (The details of this calculation are given by Gilman(1983).) The actual fluid velocity at 400°C is 2.4 times the minimum fluidization velocity while that at 1000°C is 6.6 times the minimum fluidization velocity.

The experimental procedure for the operation of the fluidized bed is as follows:

1. Weigh one 0.5 gram sample of quartz wool. Pack the cold trap with the quartz wool.

2. Weigh one 5.0 gram sample of the coal. Pour sample into

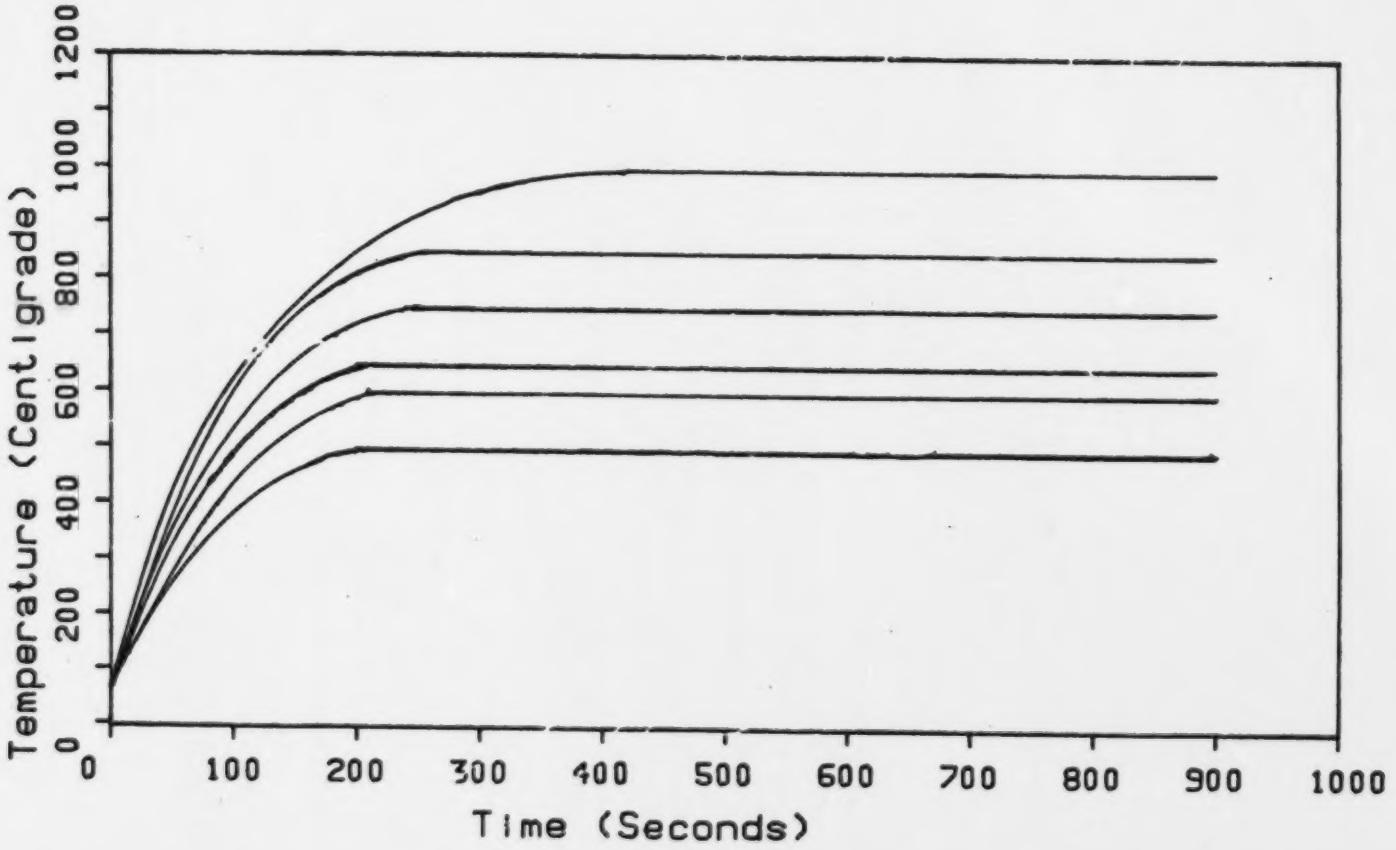

FIGURE 5 HEATING RATE CURVES FOR THE FLUIDIZED BED

reactor.

3. Set digital controller on Lindberg furnace to 50°C above the selected reactor temperature. Before the furnace reaches equilibrium perform steps 4-6.

4. Turn on helium (PCV valve). Purge the system with helium for at least 5 minutes. The purpose of this step is to ensure that no air remains in the system, so that pyrolysis, not combustion, is studied. Check for leaks in the reactor using gauge P13.

5. Turn on gas preheater. Set the dial to 1000°C.

6. Turn on both heating tapes.

7. Once furnace has reached 50°C above the selected reactor temperature open the furnace and insert the reactor. The 50°C allows for cooling of the furnace walls when the furnace is opened.

8. Close the furnace and reset the furnace temperature to the desired value.

9. Allow the pyrolysis to reach equilibrium. This takes approximately 15 minutes.

10. Collect the gases in the evacuated bomb.

11. Turn off the furnace and preheater.

12. Remove the reactor from the furnace. Allow the fluidized bed to cool to 50°C.

13. Shut off the helium.

14. Open the bed and remove the char.

15. Determine the weight of the char. Place char in a labeled storage bottle.

16. Remove quartz wool from the cold trap. Determine the weight of the tar and water.

17. Label and store the quartz wool in a desiccator. Subsequently dry and reweigh to determine the relative amounts of tar and water.

Coal Feedstocks

Pyrolysis experiments were performed on 5.0 gram samples of 10X80 mesh New Mexico Navajo Mine (NMNM) subbituminous coal, for both reactors. In addition, pyrolysis experiments were performed on 5.0 gram samples of 40X100 mesh Montana Lignite for the fluidized bed reactor. The lignite was furnished by Pennsylvania State University, College of Earth and Mineral Science, Coal Research Section. Ultimate and proximate analyses of these coals are given in Tables 2-5.

Table 2

Ultimate Analysis of New Mexico Navajo Mine Subbituminous Coal

	As-Received	Dry Basis	Dry Ash-Free Basis
Wt. % C	54.4	60.1	76.6
Wt. % H	3.5	3.9	4.9
Wt. % S	0.8	0.9	1.1
Wt. % O	12.3	13.6	17.4
Wt. % Ash	19.4	21.5	---
Wt. % Moist.	9.6	---	---

Table 3

Proximate Analysis of NMNM As-Received

Wt. % moisture	9.6
Wt. % volatile matter	33.3
Wt. % fixed carbon	37.7
Wt. % ash	19.4

Table 4

Ultimate Analysis of Partially Dried
Montana Knife River Deposit Lignite

	As-Received	Dry Basis	Dry Ash-Free Basis
Wt. % C	57.1	63.3	72.1
Wt. % H	2.7	3.0	3.4
Wt. % S	0.6	0.6	0.7
Wt. % O	18.7	20.9	23.8
Wt. % Ash	11.0	12.2	---
Wt. % Moist	9.9	---	---

Table 5

Proximate Analysis of Partially Dried
Montana Knife River Deposit Lignite

Wt. % moisture	9.9
Wt. % volatile matter	41.0
Wt. % fixed carbon	38.1
Wt. % ash	11.0

Sampling and Analysis

Two replications per temperature per reactor are performed. The flow rate of the sweep gas is set at 0.2 SCFM at a pressure of 135.35 kPa (5.0 psig). The tar, water, gases, and char are physically separated, collected, and analyzed. Descriptions of the analyses follow; further details are provided by Gilman(1983).

Char. The char is removed from the pyrolysis reactor and weighed. The difference between the weight of the feed stock and the weight of the char is the weight of the volatiles. The char is ground to a fine powder using a mortar and pestle for further analysis.

For ultimate analysis 100 mg samples of the char are weighed in glazed porcelain boats. The weight percent of carbon and hydrogen are determined following ASTM Method D-3178, and nitrogen is determined by the Kjeldahl-Gunning method. In the sulfur analysis, vanadium pentoxide

is spread over the surface of a sample and the treated sample is analyzed with a Fisher Model 470 Sulfur Analyzer. For proximate analysis of the char 1000 mg samples are weighed in quartz crucibles and analyzed with a Fisher Model 490 Coal Analyzer.

The results of these analyses are introduced into a computer program, which calculates fractional volatilization and retention for total mass and individual elements.

Tar And Water. Following pyrolysis the quartz wool is removed from the reactor and weighed to determine the weight of the tar and water. The tar and water-laden quartz wool is placed in a drying oven at 70°C for three hours to remove all moisture. The wool and dry tar are reweighed, and the mass of water collected is determined by difference. (The assumption is that a negligible amount of tar volatilizes at 70°C. Slight errors in the mass balance could result if this assumption is violated.)

The tar is analyzed for carbon and hydrogen using ASTM Method D-1378. The weight fraction of sulfur in the tar is determined using a Fisher Model 470 Sulfur Analyzer. The oxygen content of the tar is determined by difference.

ASTM Test D-3178-73, the standard test for carbon and hydrogen in the analysis of coal and coke, has been modified for coal tar analyses. The coal tar sample is prepared for analysis using the following steps:

1. The water is removed from the coal tar by placing the flask with the tar and water laden wool in a drying oven for three hours at 70°C. The flask is reweighed and the weight of the coal tar and water collected in the cold trap are determined by difference and recorded.

2. A quartz glass tube with dimensions of 3/8 inch diameter and 3 inches in length is weighed and the weight recorded. The quartz glass tubing functions as a combustion boat.

3. The quartz wool laden with dry coal tar is removed from the flask and inserted in the quartz glass tube. The total weight of the glass, wool, and tar is determined.

4. The procedure of ASTM Test D-3178-73 is followed.

5. The weight of the coal tar sample for the calculations of the carbon and hydrogen weight percents is determined from the difference between the pre-analysis total weight of quartz glass, wool, and tar less the post-analysis weight of the quartz glass and wool.

The Fisher Model 470 Sulfur Analyzer can be used to determine the weight percent of sulfur in the coal tar. The preparation procedure as described for the carbon-hydrogen analysis is followed through step 3. The next steps are listed below:

1. The procedure of sulfur analysis as outlined in the Fisher Model 470 Sulfur Analyzer is followed.

2. The weight of the dry coal tar that is determined by difference is entered as an estimated weight of the coal tar sample on the Fisher Model 470 Sulfur Analyzer. It is an estimate because some coal tar adheres to the inner glass wall of the cold trap as well as a small portion of the coal tar smears on the plastic gloves that one uses when transferring the tar-laden quartz wool from the cold trap to the quartz glass tubing.

3. The tar-laden quartz wool in the quartz glass tube is combusted and analyzed.

4. The wool is allowed to cool in a desiccator. The cooled tube with wool is weighed.

5. The correct weight of the tar sample is determined from the difference between the pre-analysis quartz tubing with tar-laden wool and the post-analysis weight of the quartz tubing with wool.

6. The weight percent of sulfur as reported by the sulfur analyzer is an estimate. It is easily corrected. The calibration curve for the sulfur weight percent is a simple linear regression with a zero intercept and a positive slope.

Gases. Evolved gases are collected in heated evacuated one-liter stainless steel or internally coated glass bombs and analyzed by gas chromatography. The gases taken represent an integrated sample of the entire period of the pyrolysis process. One of several detectors is used, depending on the species to be quantified. The analysis conditions and the species routinely measured are listed in Table 6.

A Perkin Elmer Model Sigma 10 Integrator provides a report of the integrated area attributed to each peak. The data from the integrator serve as input to a computer program, which calculates the moles of each species in the injected sample. The output of this program is in turn fed to a second program, which determines moles of each gas species per gram of feed, and the weight fraction of each gas species relative to the weight of the feed stock.

Table 6
Gas Chromatograph Settings and Species Analyzed

A. Permanent gases

Instrument	Carle Model 1158A Gas Chromatograph
Columns	1) 80% Poropak-N, 20% Poropak-Q, 8'x1/8" SS 2) 90% Mol.Sieve 13X, 10% Mol.Sieve 5A, 8'x1/8" SS
Detector	Thermal conductivity
Temperatures	Injector -- 348K, Detector -- 348K Columns -- 348K. Run columns in series for 2 min., then bypass molecular sieve column
Species	Hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, hydrogen sulfide

B. Sulfur gases

Instrument	Varian Model 3700 Gas Chromatograph
Column	60/80 Carbopak B/1.5% XE-60/1.0% H_3PO_4, 6'x1/8" teflon
Detector	Flame photometric
Temperatures	Injector - 373K, Detector - 453K Column - 3 min.@303K, ramp to 403K@288K/min, 6 min.@403K
Species	Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, carbon disulfide, thiophene

C. Aromatic hydrocarbons

Instrument	Varian Model 3700 Gas Chromatograph
Column	5% SP-1200/1.75% Bentone 34 on 100/120 Supelcoport, 6'x1/8 in SS
Detector	Flame Ionization
Temperatures	Injector - 383K, Detector - 523K Column - Ramp from 323K to 348K @ 281K/min
Species	Benzene, toluene, xylene, ethylbenzene

Table 6 (continued)

D. Aliphatic hydrocarbons

Instrument	Tracor 550 Gas Chromatograph
Columns	80/100 Porapak-QS 7'x1/8" SS followed by a 20% Carbowax 20MTPA, 60/80 Chromosorb B WAW DMCS, 10' x 1/8" SS
Detector	Flame Ionization
Temperatures	Injector - 383K, Detector - 523K Columns - Ramp from 323K to 473K @ 28lK/min, hold 2 minutes at 473K
Species	Methane, ethane, ethylene, propane, propylene, methanol, butane, butene

RESULTS

Mass Balances

Mass balances have been obtained for the pyrolysis of New Mexico subbituminous coal in the fixed bed and fluidized bed reactors and for the pyrolysis of Montana lignite in the fluidized bed reactor. The results for the fluidized bed, which served as the principal source of data in this project, are presented in Tables 7 and 8. Total mass balances for the fixed bed and elemental balances for carbon, oxygen, hydrogen, and sulfur for both reactors are given by Gilman(1983). The nitrogen content of both feedstocks is less than 1.0% on an as-received basis and is included in the oxygen elemental balances.

Balance closures for the fixed bed were on the order of 75-80%, significantly lower than those obtained for the fluidized bed, indicating that the collection of the pyrolytic products was more complete for the fluidized bed reactor. The lower collection in the fixed bed reactor can be attributed to the incomplete trapping of the water and tar and to the readsorption of evolved species in the bed of particles. Marginal amounts of the evolved species are adsorbed on the surfaces of the ceramic pyrolysis boats, staining the boats black. Periodic dismantling of the fluidized bed reactor revealed adsorption of tar on the inner walls of the exit line to the cold trap. Much less tar was found on the inner walls of the fluidized bed than in the fixed bed. Some losses might also have occurred through adsorption on the walls of the flow system tubes and the sample bombs.

At the higher operating temperatures, 800 to 1100^{o}C, the fixed bed reactor elemental mass balance closures for hydrogen and oxygen drop steadily with increasing operating temperatures, reflecting the increased formation of pyrolytic water. Subtracting the feed moisture from the total water gives yields for the pyrolytic water of 12.2% by weight on an as-received basis and 14.9% by weight on a dry, ash-free basis. This result is consistent with results of Suuberg et al. (1978), who analyzed lignite pyrolysis products and found total water (the volatilized moisture plus the chemically produced water) to be as high as 19.0% by weight of the pyrolysis products at an operating temperature of 1000^{o}C.

In almost every respect, data obtained in the fluidized bed were of higher quality than data obtained in the fixed bed. In the sections that follow, given results are from the fluidized bed unless otherwise indicated.

Table 7

Mass Balances for Fluidized Bed Pyrolysis
Weight % of 100 Grams of Feedstock (A.R.)
New Mexico Navajo Mine Subbituminous Coal

Temp°C	450	500	550	700	750	800	850	900	950	1000
Char	81.67	67.137	64.602	64.487	60.90	61.50	57.98	58.75	57.84	56.90
Tar	2.07	13.376	14.156	13.214	11.29	10.86	12.12	11.05	4.63	3.57
Water	10.01	5.687	8.161	9.764	11.61	8.98	9.69	9.92	15.87	14.615
H_2	0.003	0.0075	0.0126	0.1784	0.3248	0.4853	0.6871	0.7518	0.7626	0.797
CO	1.0588	0.7792	1.032	1.644	2.50	2.896	3.719	3.325	4.401	5.583
CO_2	1.078	1.97	2.4232	3.1024	3.168	3.6135	3.854	3.827	3.991	5.164
CH_4	0.323	0.6912	0.343	1.647	2.0832	1.885	2.4692	2.081	2.349	2.048
C_2H_4	0.0895	0.0803	0.0889	0.46614	0.6584	0.533	0.9706	0.7313	0.9884	0.6789
C_2H_6	0.0156	0.2026	0.2412	0.3813	0.3791	0.3366	0.3665	0.3315	0.2212	0.2277
C_3H_6	0.0090	0.0346	0.0756	0.1938	0.1635	0.4364	0.2732	0.2797	0.0270	0.2046
C_3H_8	0.0391	0.0174	0.0637	0.0338	0.1067	0.0429	0.0629	0.0382	0.0396	
C_4H_8	0.0064	0.02893	0.0934	0.1100	0.1057	0.3366	0.1708	0.3184	0.0245	0.1340
C_4H_{10}	0.0076	0.0053	0.0433	0.0326	0.0014	0.0024	0.0219	0.0413	0.0027	0.0533
Benzene	0.0038	0.0048	0.0095	0.0172	0.0339	0.029	0.0605	0.0591	0.0813	0.0380
Toluene	0.0059	0.0029	0.0070	0.0135	0.0247	0.022	0.0393	0.0374	0.0415	0.0189
Xylene	0.0048	0.0040	0.0065	0.0053	0.0071	0.0107	0.0173	0.0156	0.0049	0.0064
H_2S	0.0021	0.0731	0.0679	0.0557	0.0622	0.0864	0.1021	0.067	0.0477	0.0400
COS	0.0028	0.0046	0.0069	0.0069	0.0055	0.0053	0.007	0.0068	0.0073	0.0050
CH_3SH	-	0.0049	0.0058	0.0045	0.0037	0.0049	0.0056	0.0049	0.0020	0.0036
CS_2	-	-	-	-	-	-	0.0005	0.001	0.001	0.0005
Thiophe	-	0.0005	0.0012	0.0022	0.0019	0.0023	0.0027	0.0016	0.0097	0.0085
TOTAL	96.36	90.13	91.40	95.21	93.36	92.13	92.60	91.66	91.34	90.13

Table 8

Mass Balances for Fluidized Bed Pyrolysis
Weight % Of 100 Grams of Feedstock (A.R.)
Montana Lignite Savage Mine

Temp°C	450	500	600	650	750	800	950	1000
Char	81.170	67.609	62.476	60.688	59.294	53.670	51.742	50.770
Tar	0.00	0.597	0.510	0.520	0.112	1.33	0.411	0.129
Water	10.691	9.453	14.406	13.609	10.393	14.75	14.702	12.373
H_2	0.0108	0.016	0.220	0.317	0.679	0.870	0.801	1.401
CO	0.7613	1.328	1.94	2.481	5.934	9.981	8.420	13.104
CO_2	4.2826	6.273	11.065	9.151	11.566	9.981	10.483	9.409
CH_4	0.286	0.420	0.635	0.800	1.750	1.628	2.011	2.303
C_2H_4	0.0185	0.0858	0.195	0.2658	0.6532	0.501	0.756	0.476
C_2H_6	0.0232	0.134	0.225	0.2916	0.2813	0.1636	0.1183	0.0914
C_3H_6	0.022	0.040	0.1625	0.0475	0.2304	0.1078	0.0927	0.0317
C_3H_8	0.0348	0.0285	0.0733	0.0506	0.0464	0.0152	0.0144	0.0064
C_4H_8	0.0100	0.0277	0.123	0.0343	0.1754	0.0659	0.0865	0.0946
C_4H_{10}	0.0098	0.0183	0.0514	0.0076	0.0328	0.0092	0.0069	-
MEOH	-	-	0.0442	0.0035	0.1121	0.050	0.0525	0.0524
Benzene	-	-	0.0132	0.0201	0.0501	0.0255	0.2122	0.4750
Toluene	-	-	0.0185	0.0266	0.0359	0.0152	0.0950	0.190
Xylene	-	-	0.0140	0.0192	0.0161	0.0040	0.0349	0.0548
H_2S	0.0098	0.0166	0.016	0.0269	0.0174	0.0276	0.0363	0.0089
COS	0.0012	0.0024	0.0038	0.0054	0.0092	0.0035	0.0039	0.0026
CH_3SH	-	0.0027	0.00375	0.0070	0.0049	0.0040	0.00346	-
C_2H_5SH	0.0008	0.0010	0.0029	0.0012	0.0026	0.0005	0.0005	-
CS_2								
Thiophene	0.0002	0.0007	0.0033	0.0042	0.0049	0.0043	0.0048	0.0042
Total	97.31	86.05	92.20	88.38	91.40	90.35	90.09	90.98

Pyrolytic Weight Loss

Plots of asymptotic (long-time) weight loss vs. temperature for the slow pyrolysis of subbituminous coal in the fixed and fluidized bed (Figure 6) and of both subbituminous coal and lignite in the fluidized bed (Figure 7) exhibited a distinct pattern of devolatilization. At temperatures less than 400°C, no devolatilization occurred; only the moisture in the feedstock was volatilized. Between 400 and 700°C the major fraction of volatile material was released. Increases in temperature above 700°C produced marginal increases in asymptotic weight loss. Figure 6 shows a greater extent of devolatilization in the fluidized bed than in the fixed bed. This result is probably attributable to readsorption of volatiles on the particles in the fixed bed.

Table 9 lists experimental parameters for five studies of slow pyrolysis, including the present study. Plots of asymptotic weight loss vs. temperature based on data from these studies fall very close to a single curve over a temperature range of 400-1000°C (Figure 8). Linear regression was used to obtain a polynomial fit of the data shown in Figure 8, with the following result:

$$\text{Weight Loss (d.a.f.)} = -49.0 + 0.20T(C) - 1.066\times10^{-4}T(C)^2 \qquad (1)$$

where T(C) = temperature in degrees Celsius.

Table 9

Slow Pyrolysis
Experimental Techniques and Conditions

Investigator	Technique	Residence Time, min	Heating Rate, °C/s	Coal Feedstock
Kobayashi (1976)	Crucible	20 - 90	1 - 5	Montana Lignite
		20 - 90	1 - 5	Pittsb. Seam Bittum.
Agreda (1979)	Batch	20	5 - 45	Montana Subbit.
Gilman	Fixed Bed	10	1.5 - 6	NMNM Subbit.
Gilman	Fluidized Bed	15	2.2 - 2.4	NMNM Subbit.
		15	2.2 - 2.4	Montana Savage Lig.

Asymptotic weight loss data for rapid pyrolysis (10^3-10^5 °C/s) were obtained from the literature. Sources for these data are listed in Table 10.

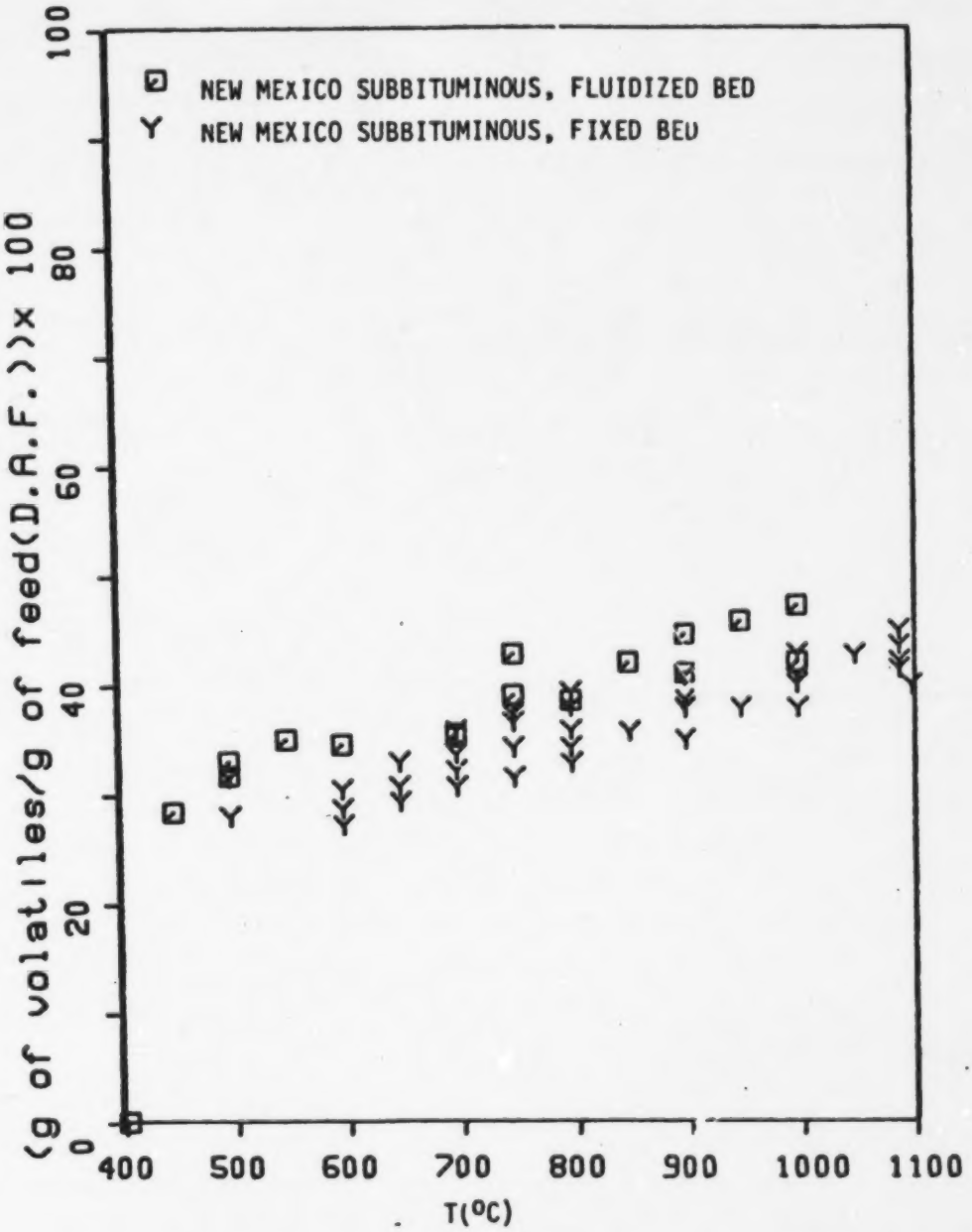

FIGURE 6 FRACTIONAL DEVOLATILIZATION OF SUBBITUMINOUS COAL IN FIXED AND FLUIDIZED BED REACTORS

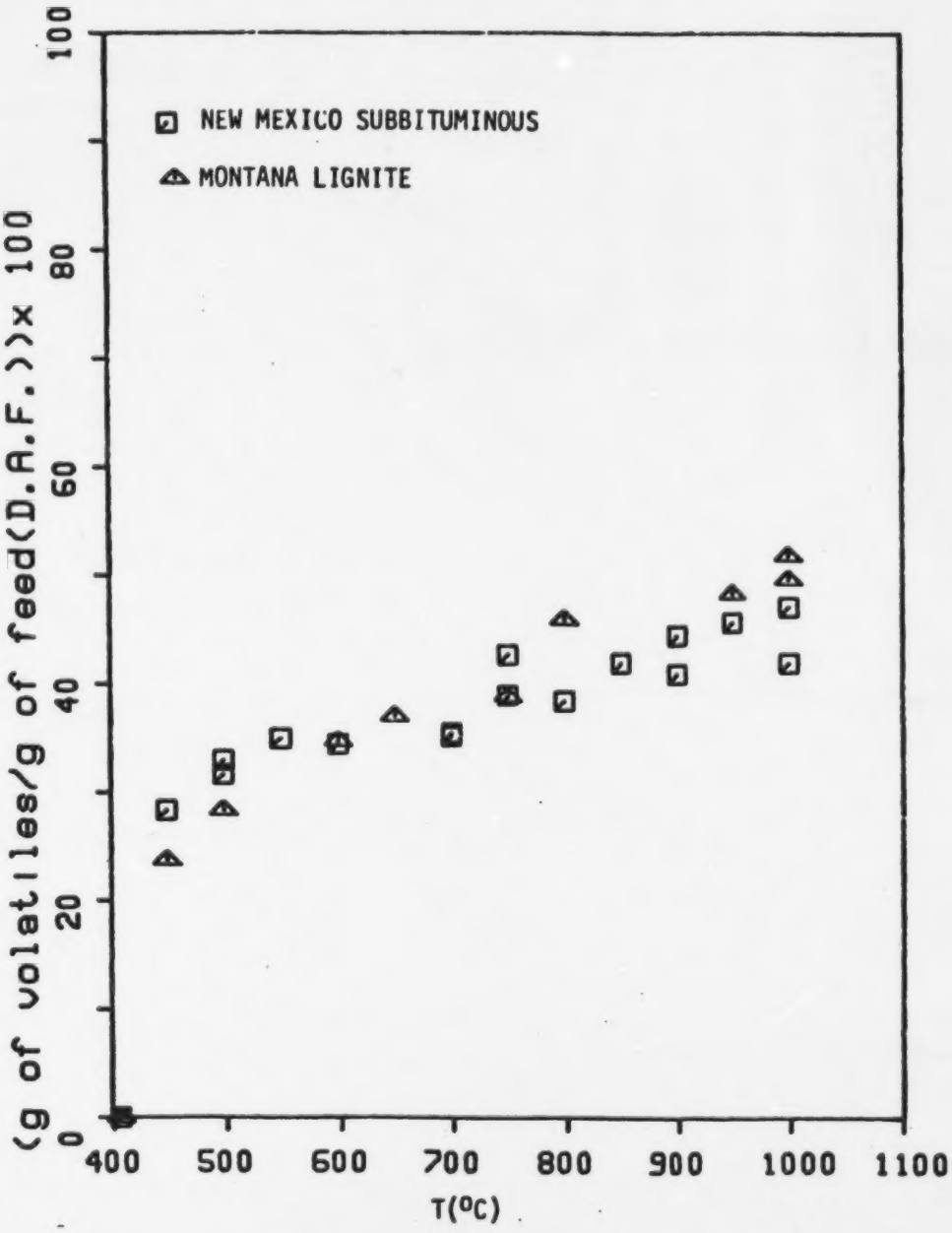

FIGURE 7 FRACTIONAL DEVOLATILIZATION OF SUBBITUMINOUS AND LIGNITE COALS IN THE FLUIDIZED BED REACTOR

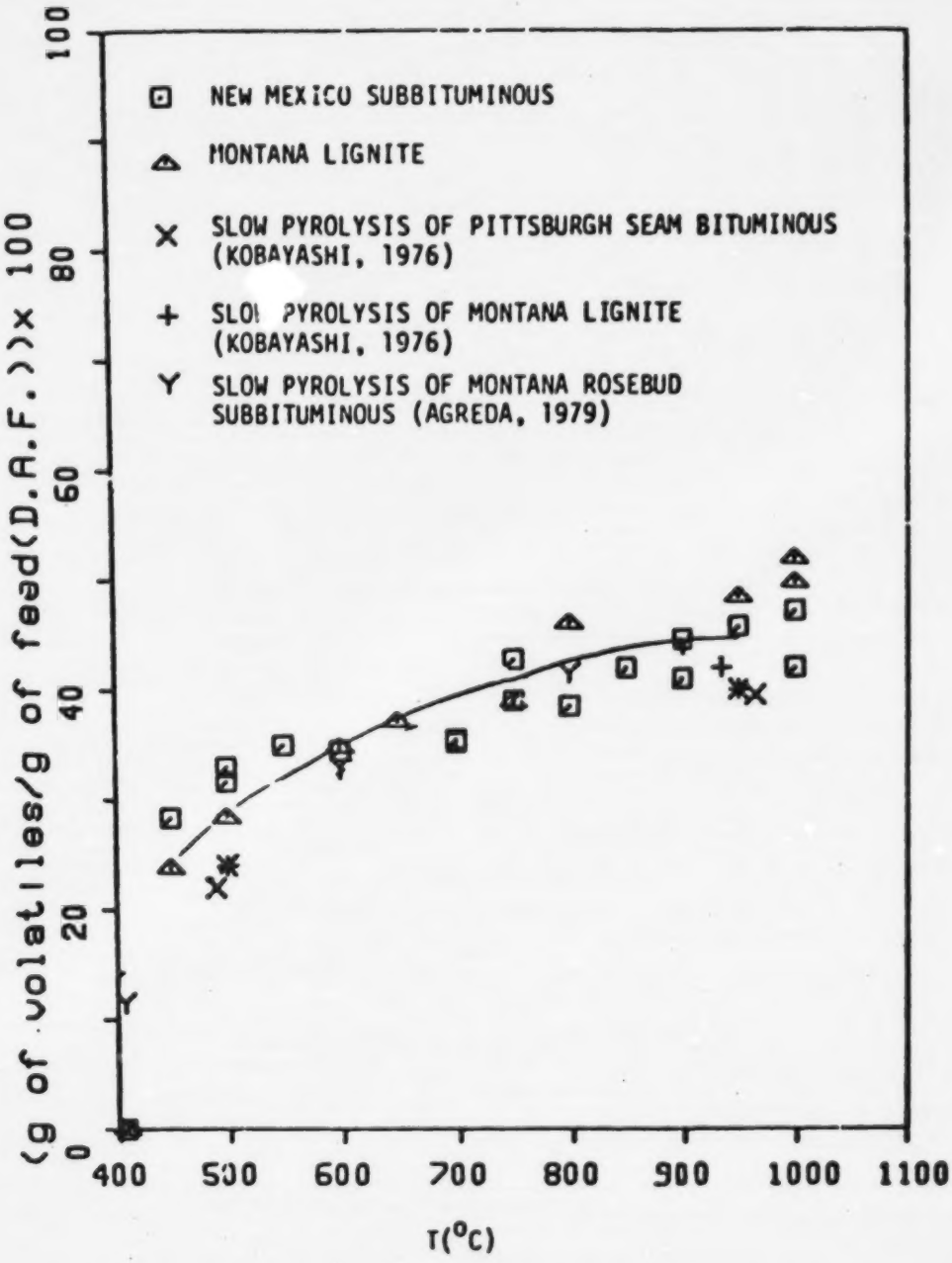

FIGURE 8 FRACTIONAL DEVOLATILIZATION IN THE SLOW PYROLYSIS OF FIVE COALS

Table 10

Rapid Pyrolysis
Experimental Techniques and Conditions

Investigator	Technique	Residence Time	Heating Rate, $^{o}C/s$	Coal Feedstock
Kobayashi (1976)	Laminar Flow	200msec	10^4-$2X10^5$	Montana Lignite
	Laminar Flow	200msec	10^4-$2X10^5$	Pitts. Seam Bit.
Agreda (1979)	Laminar Flow	1500msec	$3X10^3$-10^4	Mon. Subbit.
Suuberg (1978)	Wire Screen	<30sec	10^2-10^4	Montana Lignite
Suuberg (1979)	Wire Screen	<30sec	10^2-10^4	Pitts. Seam Bit.

In Figure 9, asymptotic weight loss is plotted versus temperature for both fast and slow pyrolysis, with the data for fast pyrolysis being taken from the references in Table 10. The data for each heating regime show a surprising independence of coal rank; apparently, the fractional asymptotic weight loss depends only on temperature and whether the heating is slow or fast, but not on which coal is being pyrolyzed. Moreover, the curves for the two regimes are seen to be distinctly different. Apparent weight losses for fast pyrolysis are lower than those for slow pyrolysis over the temperature range of 400-900^{o}C. Between 900 and 1000^{o}C, apparent weight losses are similar.

The data for rapid pyrolysis shown on Figure 9 were fitted by nonlinear regression to obtain the following formula:

$$\text{Weight Loss (d.a.f.)} = 165 \exp[-0.000714\ T(C)] - 846 \exp[-0.00310\ T(C)] + 1350 \exp[-0.00587 T(C)] \qquad (2)$$

where T(C) = temperature in degrees Celsius. The curves shown on Figure 9 are plots of Equations (1) and (2).

For ease of reference, analyses of the coals for which data are given in Figure 9 are summarized in Table 11.

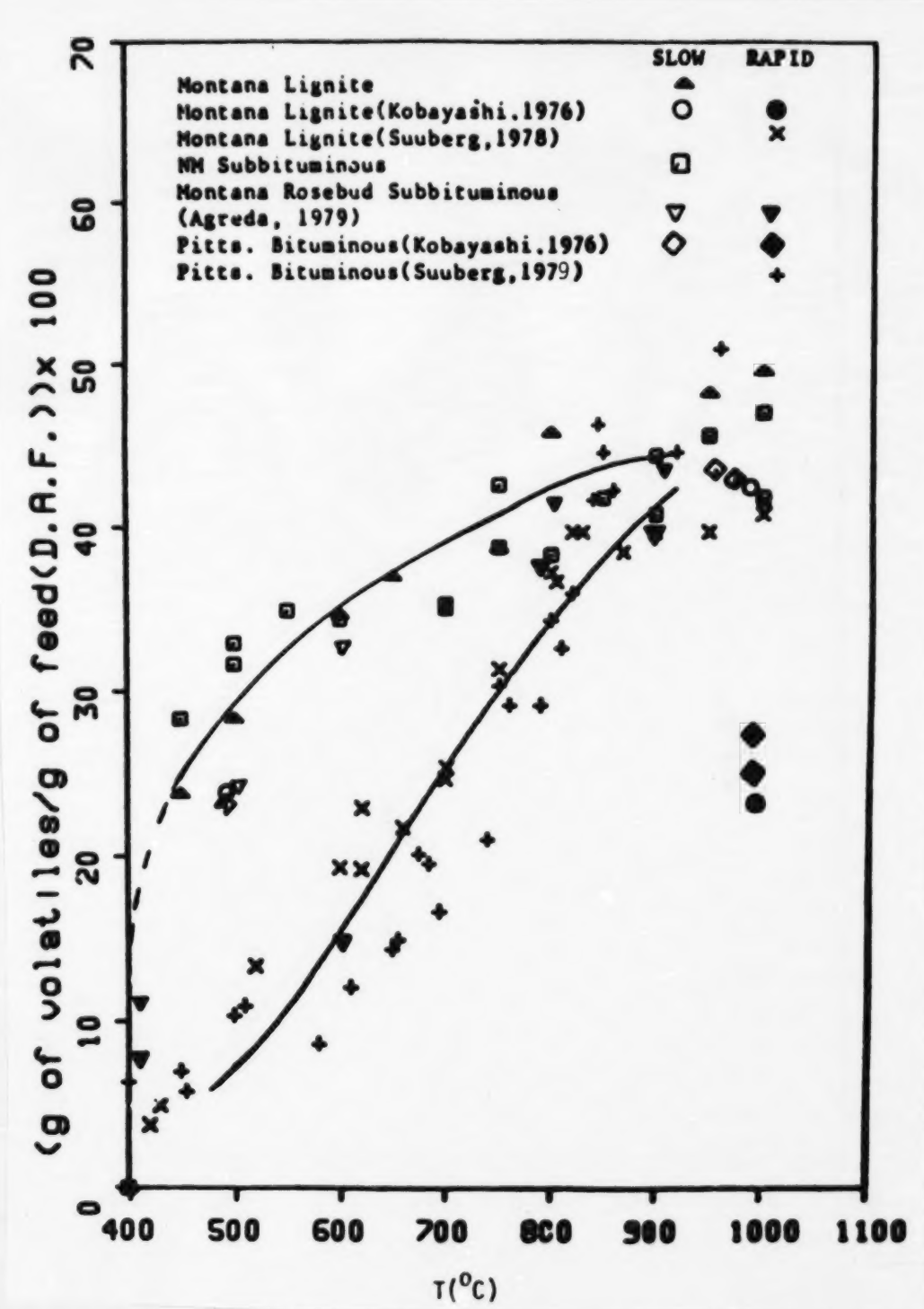

FIGURE 9. FRACTIONAL DEVOLATILIZATION IN THE SLOW AND RAPID PYROLYSIS OF SEVERAL COALS

Elemental Release

Plots of asymptotic oxygen and hydrogen volatilizations versus temperature (Figures 10 and 11) show oxygen and hydrogen volatilizations increased with temperature over the range 400-1000°C; 80% of both oxygen and hydrogen were volatilized at 800°C, and 90% were volatilized at 900°C. Similar results are reported by Kobayashi (1976) for slow pyrolysis and by Suuberg et al. (1978) for rapid pyrolysis.

A lower fractional volatilization of carbon was found than was observed for hydrogen and oxygen. The maximum volatilization of carbon, approximately 35% by weight of the feed carbon, was observed at 1000°C for the subbituminous feedstock. For slow heating rates (Figure 12), a greater fraction of the feed carbon was volatilized from the subbituminous and bituminous feedstocks than from lignite. As Figure 13 illustrates, rapid pyrolysis produced lower volatilization of carbon than did slow pyrolysis for similar lignite feedstocks.

Asymptotic sulfur volatilization increased with temperature for the pyrolysis of subbituminous coal in the fixed bed, approaching a fractional release of 50% at temperatures above 900°C. This finding closely agrees with results Kobayashi (1976) presents for crucible pyrolysis of lignite and bituminous coals (Figure 14). In contrast, plots of fractional sulfur volatilization in the fluidized bed pyrolysis of lignite and subbituminous coal exhibit maxima in the temperature range 600-800°C (Figure 15). The latter finding is consistent with the observation of Attar (1978) that the sulfur content of coke reaches a minimum around 700 to 800°C. The production of hydrogen sulfide, the major volatile sulfur species, recommences only around 1100°C.

Several factors might account for the observed maxima in the sulfur volatilization curves. At temperatures above about 750°C, internal sintering of coal begins to take place, leading to a lowered porosity and a decreased ability of the H_2S evolved to escape. At the same time, the evolved H_2S reacts to an increasing extent with such mineral constituents of coal as calcium, iron, and magnesium oxides and carbonates, forming sulfides and thereby retaining the sulfur in the char.

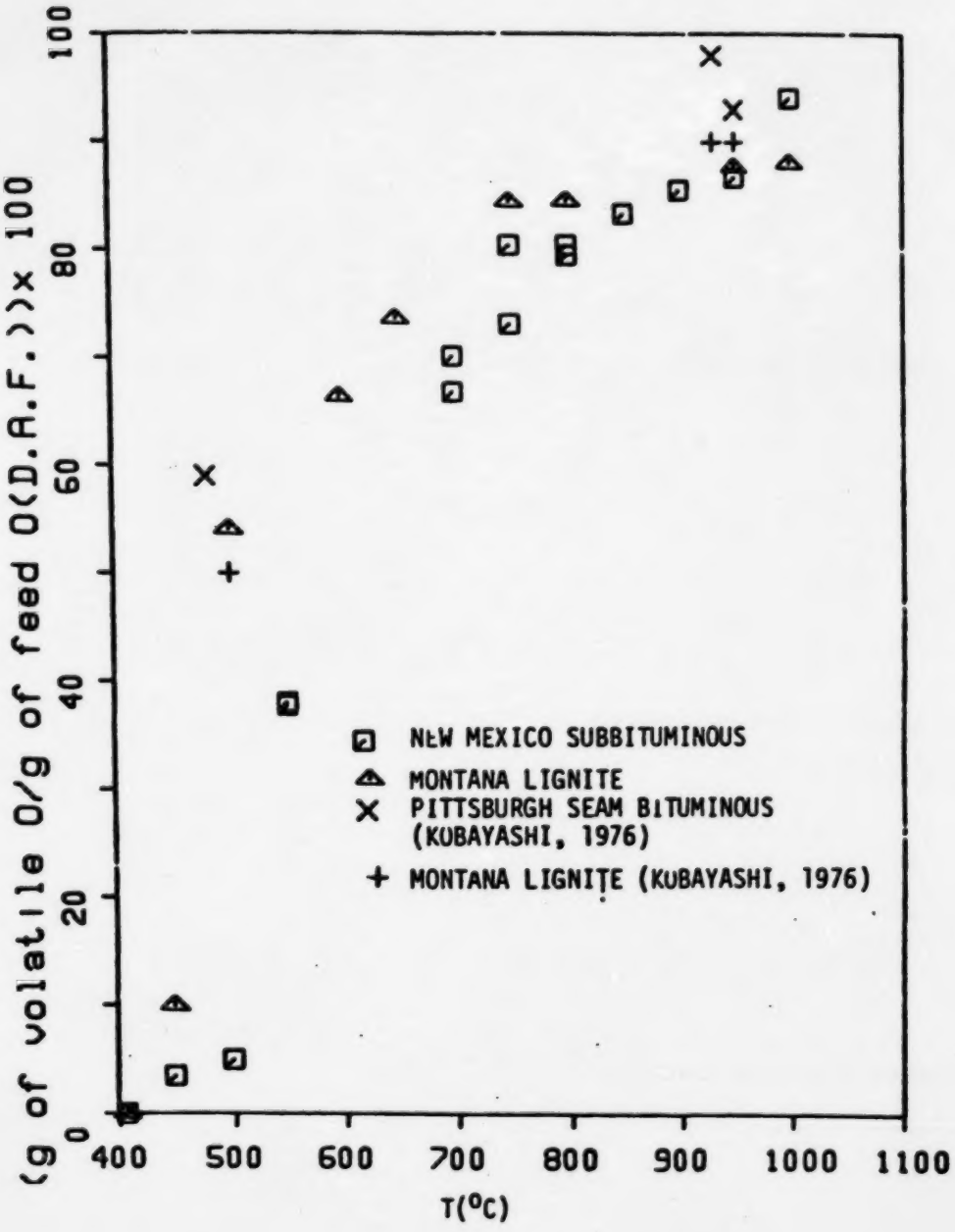

FIGURE 10 FRACTIONAL RELEASE OF OXYGEN IN THE SLOW PYROLYSIS OF FOUR COALS

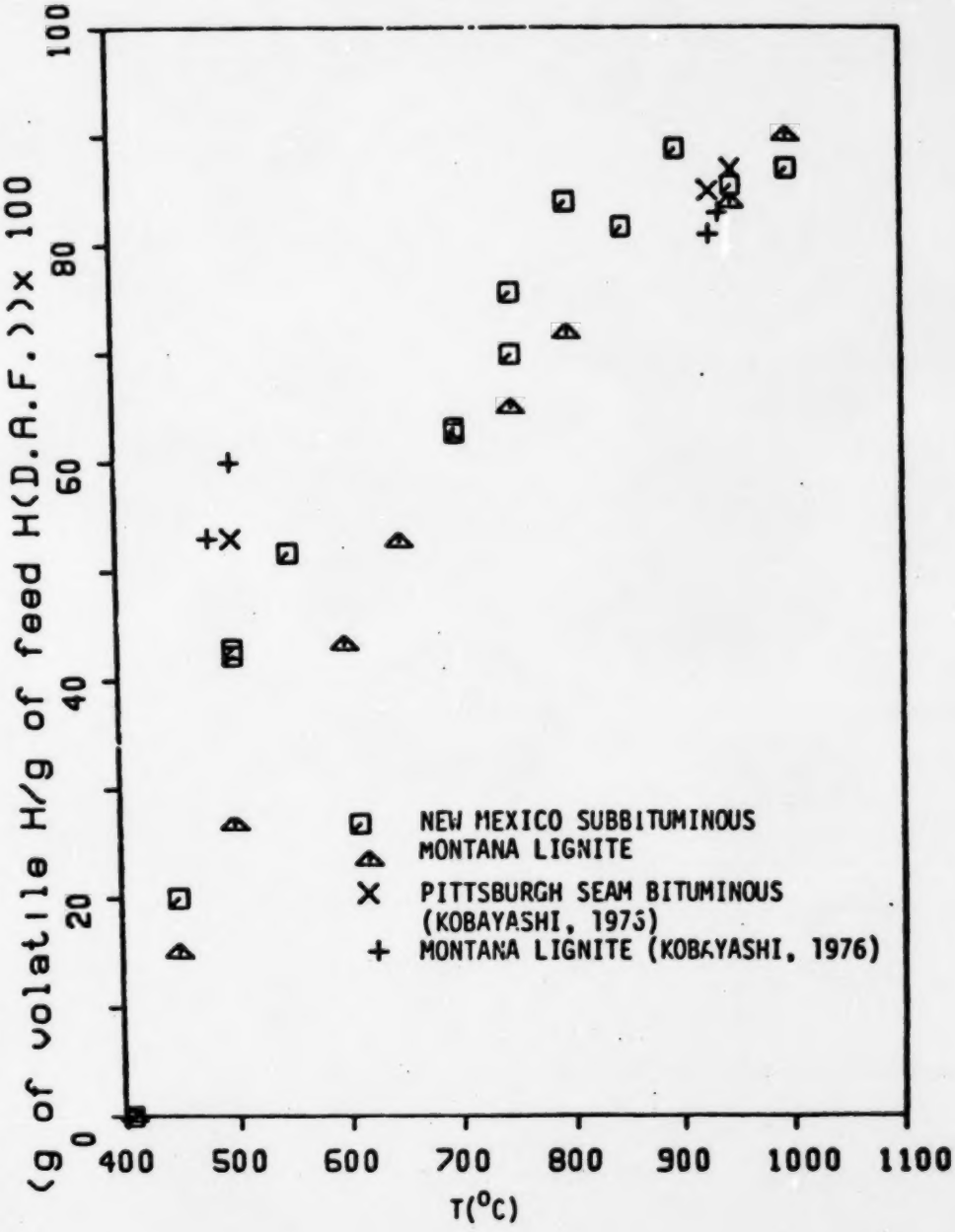

FIGURE 11 FRACTIONAL RELEASE OF HYDROGEN IN THE SLOW PYROLYSIS OF FOUR COALS

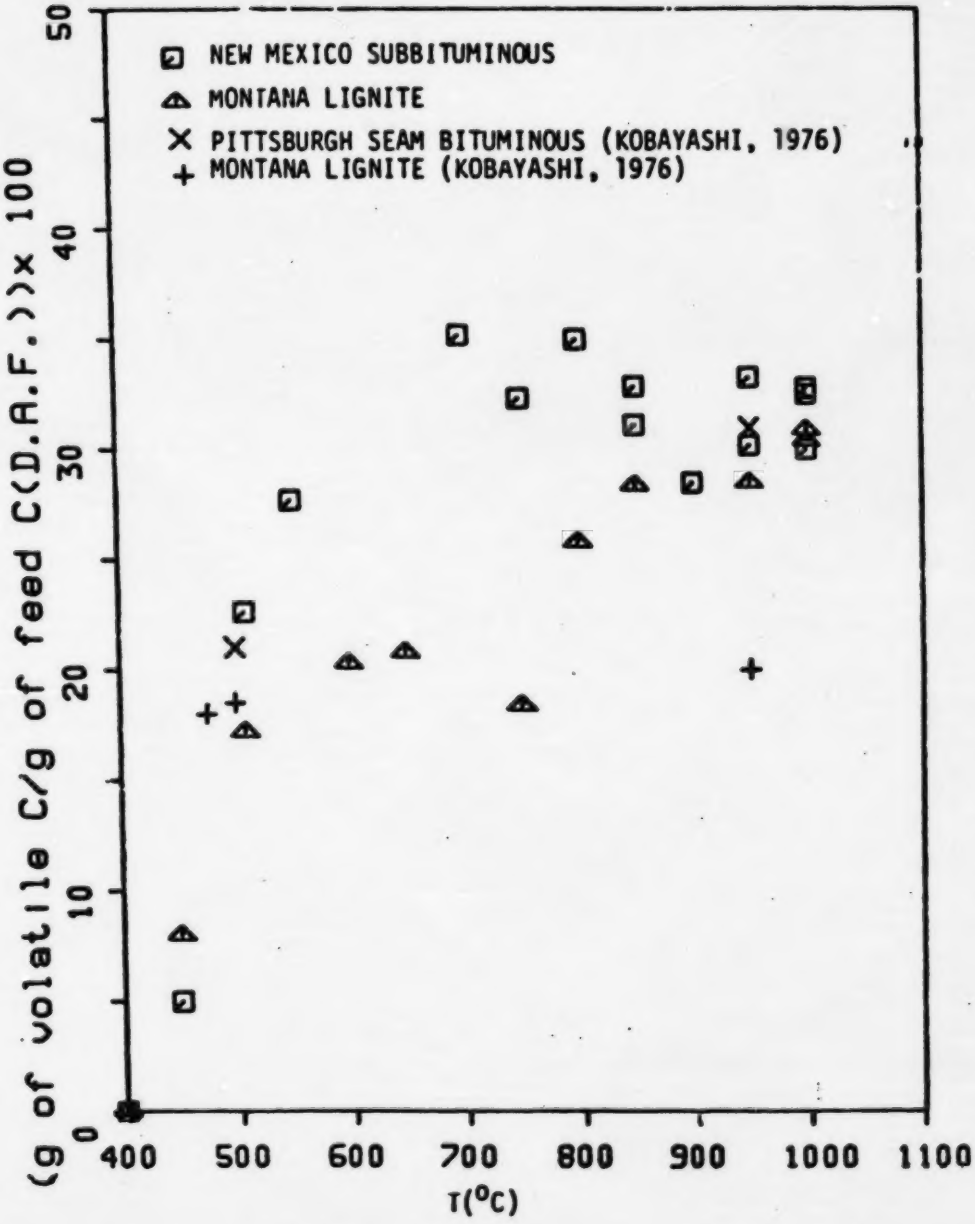

FIGURE 12 FRACTIONAL RELEASE OF CARBON IN THE SLOW PYROLYSIS OF FOUR COALS

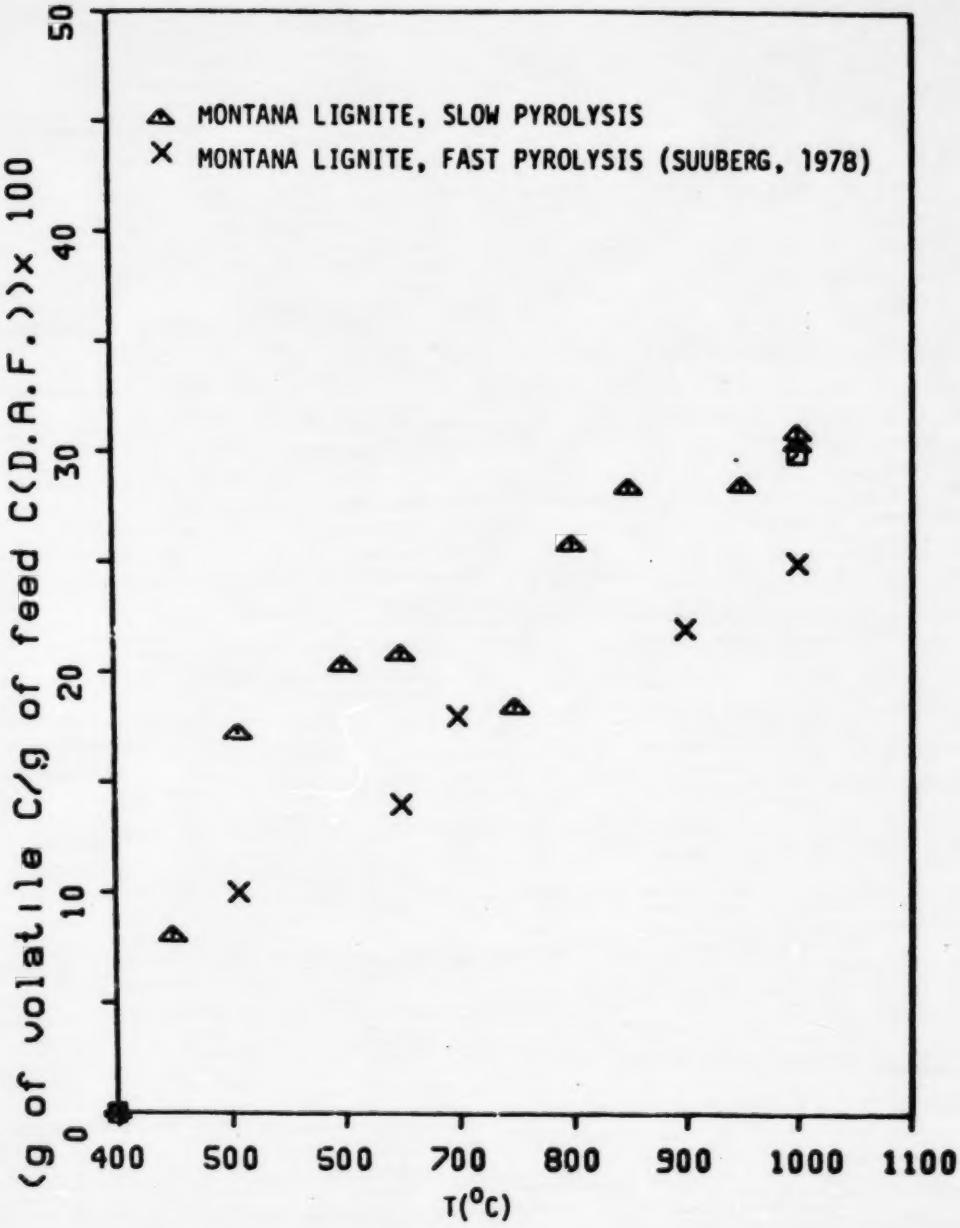

FIGURE 13 FRACTIONAL RELEASE OF CARBON IN THE SLOW AND RAPID FAST PYROLYSIS OF LIGNITE

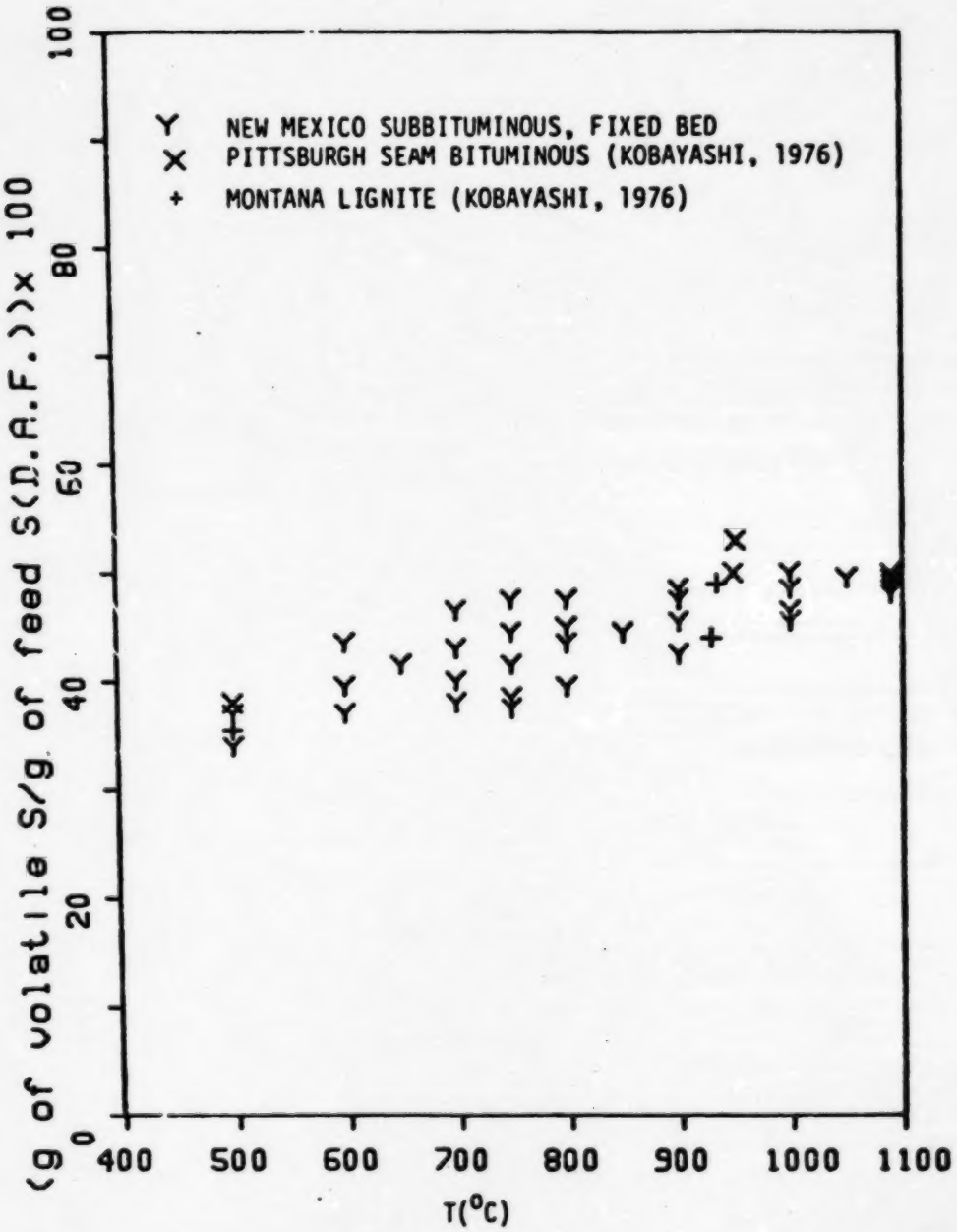

FIGURE 14 FRACTIONAL RELEASE OF SULFUR IN THE SLOW FIXED BED PYROLYSIS OF THREE COALS

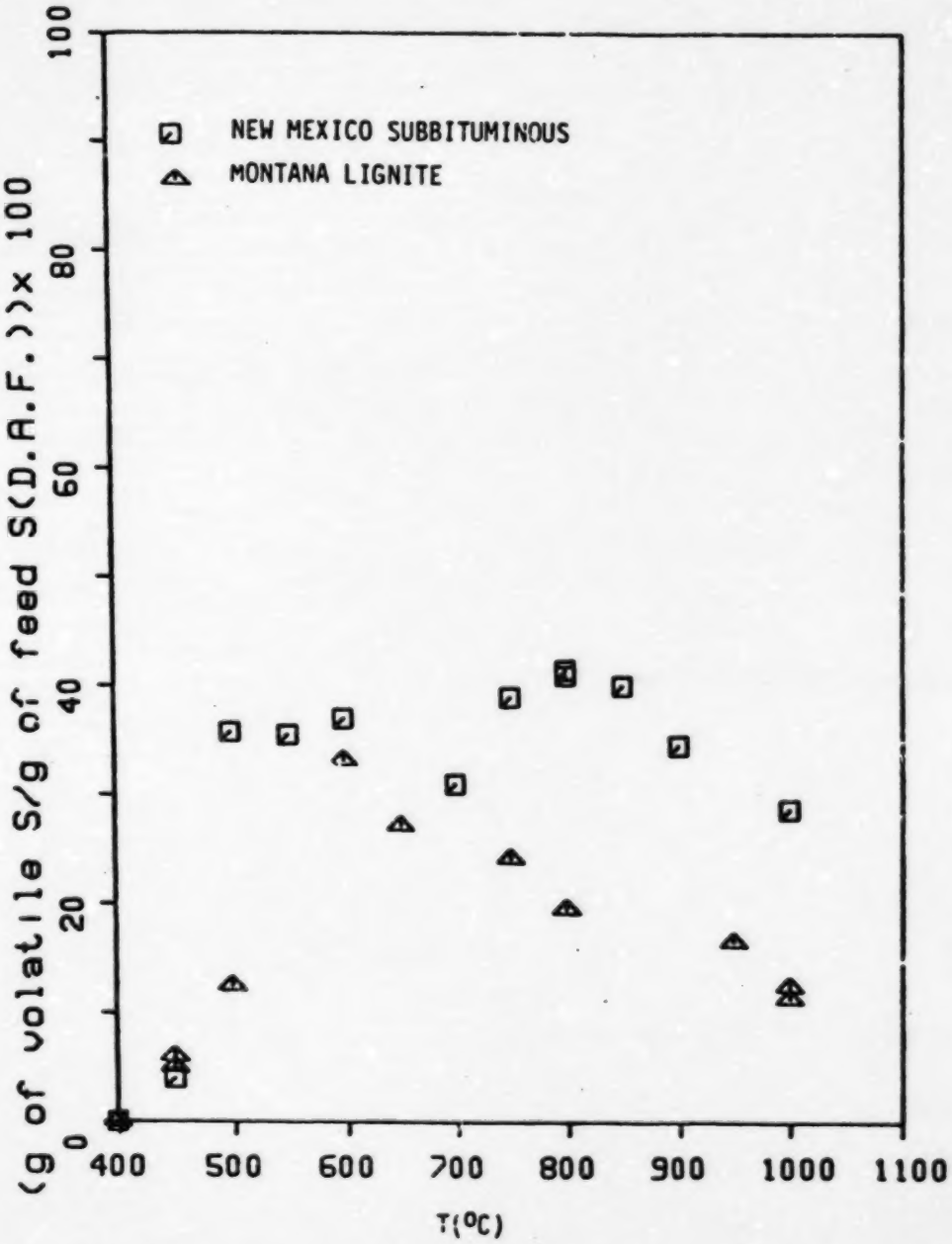

FIGURE 15 FRACTIONAL RELEASE OF SULFUR IN THE SLOW FLUIDIZED BED PYROLYSIS OF TWO COALS

Table 11

Coal Characterization Data
Elemental Analysis Reported on Dry Ash-Free Basis
Proximate Ash And Moisture Reported on an As-Received Basis

Coal	C	H	O*	S	Ash	Moisture
A	76.6	4.9	17.3	1.1	19.4	9.6
B	72.1	3.4	23.8	0.7	11.0	9.9
C	77.7	5.0	15.9	1.3	24.9	7.9
D	77.9	9.9	11.3	0.8	8.9	21.9
E	77.9	5.8	11.0	5.6	10.8	2.2
F	69.3	6.3	22.7	1.1	7.8	13.6
G	71.2	4.6	22.9	1.3	9.9	6.8
H	77.7	5.5	10.8	6.1	11.3	1.4
I	82.0	5.4	10.8	2.4	---	--
J	68.3	4.6	26.5	1.2	---	--

* Nitrogen included with oxygen.

where A = New Mexico Navajo Mine Subbituminous Coal
B = Montana Knife River Deposit Lignite
C = North Barber No.8 Subbituminous Coal(Agreda, 1979)
D = Montana Rosebud Subbituminous Coal(Agreda, 1979)
E = Pittsburgh Seam No.8 Subbituminous Coal(Kobayashi, 1976)
F = Montana Lignite-A(Kobayashi, 1976)
G = Montana Lignite, Savage Mine, Knife River (Suuberg, 1978)
H = Pittsburgh Seam No.8 Bituminous Coal(Suuberg, 1979)
I = Pittsburgh Seam Bituminous Coal(Solomon, 1979)
J = Montana Lignite(Solomon, 1979)

Agreda et al.(1979) report that North Barber No. 8 Subbituminous Coal, a coal very similar to the New Mexico Navajo Mine Subbituminous Coal, contains negligible sulfatic sulfur, 42.5% of the total sulfur as pyritic sulfur, and 57.5% as organic sulfur. The sulfur analysis of the Montana lignite reported by Pennsylvania State University College of Earth and Mineral Sciences shows the pyritic sulfur to account for 18.2%, the sulfatic sulfur 10.9%, and the organic sulfur 70.9% of the total sulfur. The higher organic sulfur content in the lignite feed appears to have been trapped in the coal matrix by the thermal effects of pyrolysis.

Production of Tar and Water

Figure 16 shows the normalized rates of production of tar and several gas species in the pyrolysis of subbituminous coal. Tar is seen to be the major volatile species formed, with production reaching a maximum at 600-700°C. Tar production from the lignite was much lower (Figure 17). Suuberg et al.(1979) found tar production from bituminous coal as much as four times greater than from lignite.

At temperatures greater than 600-700°C the production of tar in the fluidized bed pyrolysis of both subbituminous coal and lignite diminished. The drop in tar production due to the cracking of the tar resulted in an increase in the gas fraction of the volatiles. In contrast, the production of tar from rapid pyrolysis of both lignite and bituminous in Suuberg's wire screen mesh (1979) increased with temperature. Rapid pyrolysis in the temperature range 400-1000°C does not crack the tar as does slow pyrolysis.

Carbon volatilization was found to be greater for bituminous and subbituminous coals than for lignite, yet lignite is of lower rank and is less aromatic in structure than either subbituminous or bituminous coals. This result, taken in conjunction with the relatively high oxygen content of the lignite, supports an observation of Gavalas (1981) that the oxygen content of the feedstock acts to suppress tar yields. Gavalas proposes the following phenolic condensation mechanism:

$$\text{Ph-OH} + \text{Ph'-OH} \longrightarrow \text{Ph-O-Ph'} + H_2O$$

$$\text{Ph-CH} + \text{Ph'-OH} \longrightarrow \text{Ph-C-Ph'} + H_2O.$$

The reaction of two hydroxyl groups produces a molecule of water and an ether bridge. Ether bridges are thermodynamically very weak. The breaking of the ether bridge leads to the volatilization of the second oxygen atom. The hydroxyl group that reacts with the benzyl radical forms a methylene bridge, and the oxygen is released in the water molecule. The cross-links formed between aromatic structures in this process are strong enough to inhibit the release of aromatic fragments as tars.

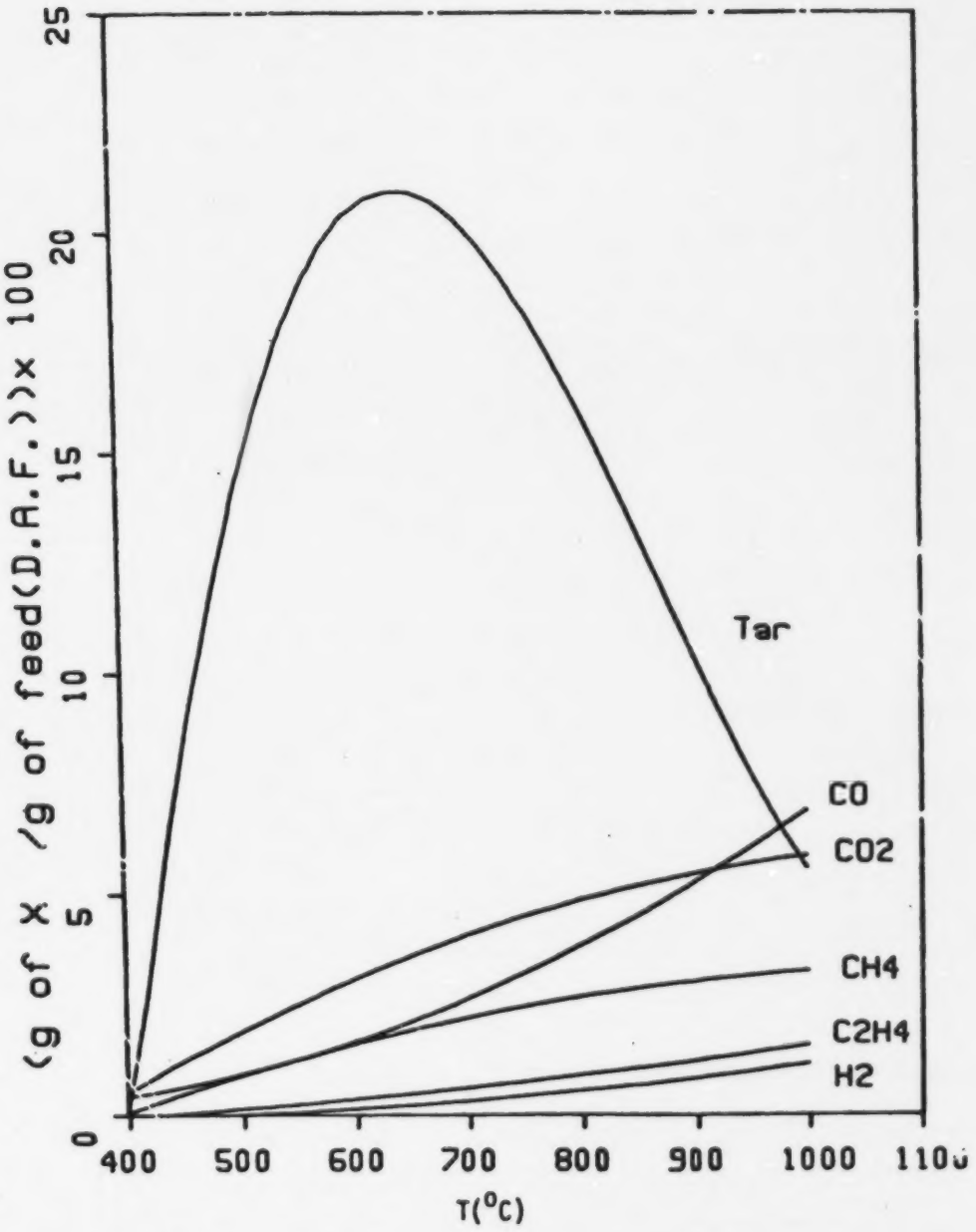

FIGURE 16 YIELDS OF TAR AND GASES IN THE PYROLYSIS OF SUBBITUMINOUS COAL

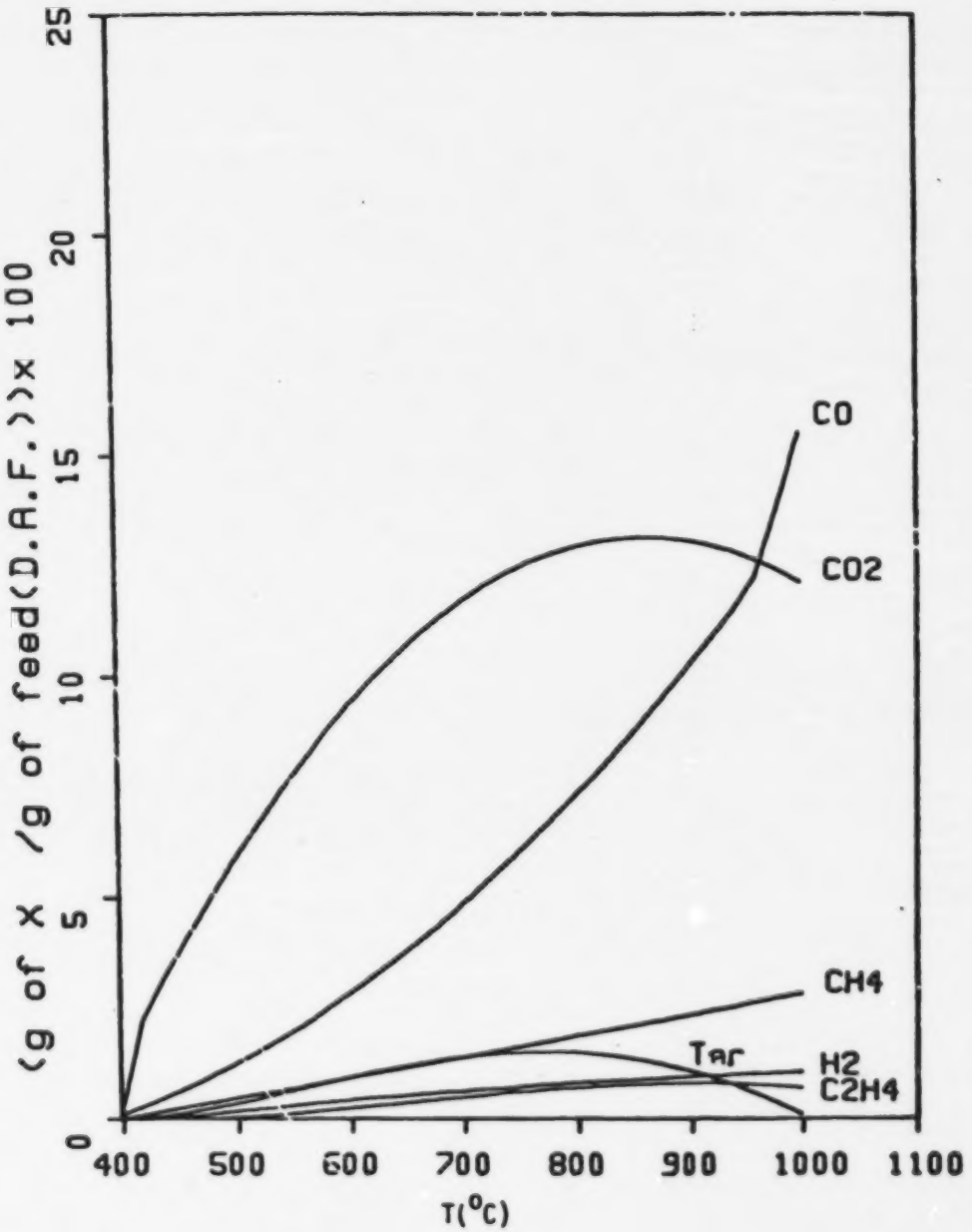

FIGURE 17 YIELDS OF TAR AND GASES FROM THE PYROLYSIS OF LIGNITE

The production of water from the pyrolysis of lignite in the fluidized bed was found to be greater than that from subbituminous coal. Suuberg et al.(1979) obtained a similar result in the rapid pyrolysis of lignite and bituminous coal. The production of pyrolytic water for the fluidized bed pyrolysis of lignite decreased at temperatures greater than 800°C. Solomon (1979) observed a similar decrease in the production of water for the rapid pyrolysis of a lignite.

Overall mass, oxygen, and hydrogen balances for fluidized bed pyrolysis of lignite are presented by Gilman(1983). The balances for temperatures greater than 800°C support the observation that volatilized oxygen shifts from pyrolytic water to carbon monoxide as the temperature increases, reflecting the increasing rate of the steam-char reaction yielding carbon monoxide and hydrogen.

Tar-to-Gas Ratio

Tar-to-gas ratios are shown in Table 12 for the slow and rapid pyrolysis of several coals. In the temperature range 500-1000°C, tar-to-gas ratios dropped with increases in temperature for both subbituminous coal and lignite in the fluidized bed.

Table 12
Tar-to-Gas Mass Ratios

Temperature (C)	500	600	700	800	900	1000
Slow Pyrolysis						
NMNM Subbituminous	1.4	1.2	1.0	0.6	0.5	0.1
Montana Lignite (PSU)	0.03	0.02	0.01	0.04	0.02	0.003
Rapid Pyrolysis						
Montana Lignite*	0.9	0.3	0.2	0.2	0.2	0.2
Pittsburgh Bituminous**	1.5	2.0	2.0	1.8	1.8	1.4
Montana Lignite**	0.7	0.5	0.9	0.9	0.6	0.6

* Suuberg et al., 1978
** Solomon, 1979

Tar-to-gas ratios decrease with increasing temperature for both rapid and slow pyrolysis. The higher ratios for rapid pyrolysis as compared to slow pyrolysis of similar coals are due to the higher production of tar from rapid pyrolysis. Anthony and Howard (1976) claim that rapid heating increases the tar formation relative to the light, gas fraction. A comparison of tar-to-gas ratios from rapid pyrolysis with those from slow pyrolysis (Table 12) supports this assertion.

Pyrolytic Gases

Evolved gases were collected in evacuated one-liter stainless steel bombs and analyzed by gas chromatography. The species routinely measured were permanent gases, aliphatic hydrocarbons, aromatic hydrocarbons, and sulfur gas species.

Hydrogen, Carbon Dioxide, Carbon Monoxide, Methane, and Ethylene. Plots of asymptotic primary gas yields vs. temperature for the fluidized bed pyrolysis of subbituminous coal and lignite are presented in Figures 16 and 17, respectively. (For clarity of presentation, the data points are omitted in these figures. They are given in subsequent plots.) For both coals, asymptotic yields of hydrogen, carbon monoxide, and methane increased with temperature. Carbon dioxide was the principal gaseous product at most temperatures studied. The carbon dioxide production increased with temperature up to 900°C, and then leveled off for subbituminous coal and decreased for lignite. Carbon monoxide was the most abundant gas species above 900°C.

Comparing carbon oxide yields from the fluidized bed pyrolysis of the two feedstocks shows that greater yields of carbon monoxide and carbon dioxide were produced from lignite than from subbituminous coal. Suuberg et al.(1979) and Solomon (1979) report similar results for rapid pyrolysis. The yields of carbon monoxide and carbon dioxide for subbituminous and lignite fluidized bed pyrolysis are compared with yields reported by Suuberg in Figures 18 and 19. Heating rate apparently has little effect on CO formation, while more CO_2 is obtained in slow pyrolysis.

Yields of hydrogen were similar for both subbituminous coal and lignite in the fluidized bed. The comparison is presented in Figure 20. Solomon (1979) found similar rapid pyrolysis yields of hydrogen for bituminous coal and lignite. Greater yields of hydrogen were obtained from rapid pyrolysis than from slow pyrolysis of lignite (Figure 21).

The production of methane in the fluidized bed (Figure 22) increased with temperature, with greater yields from subbituminous coal than from lignite. As illustrated in Figure 23, the yields of methane were greater for slow pyrolysis than fast pyrolysis.

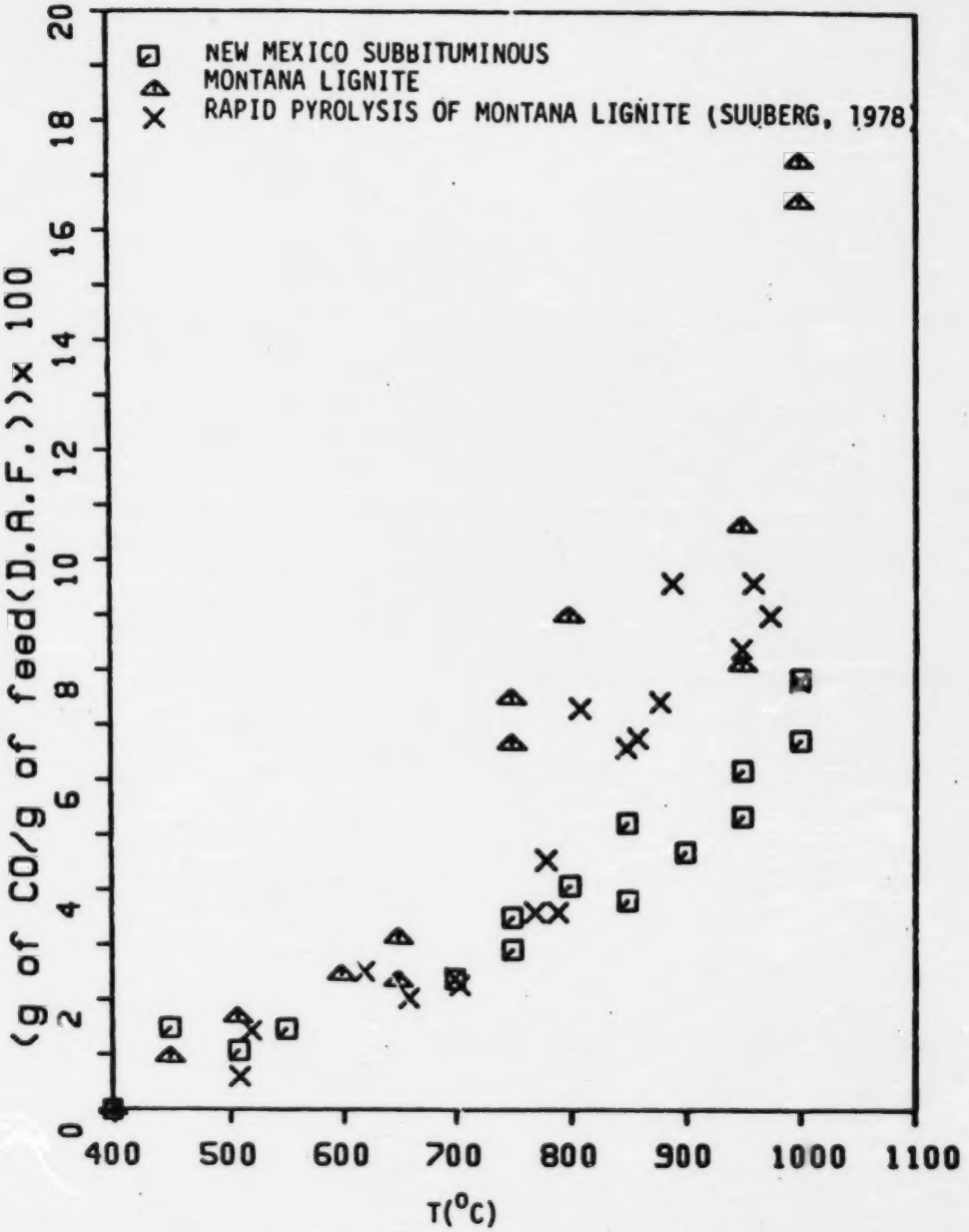

FIGURE 18 YIELDS OF CARBON MONOXIDE FROM THE SLOW AND RAPID PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

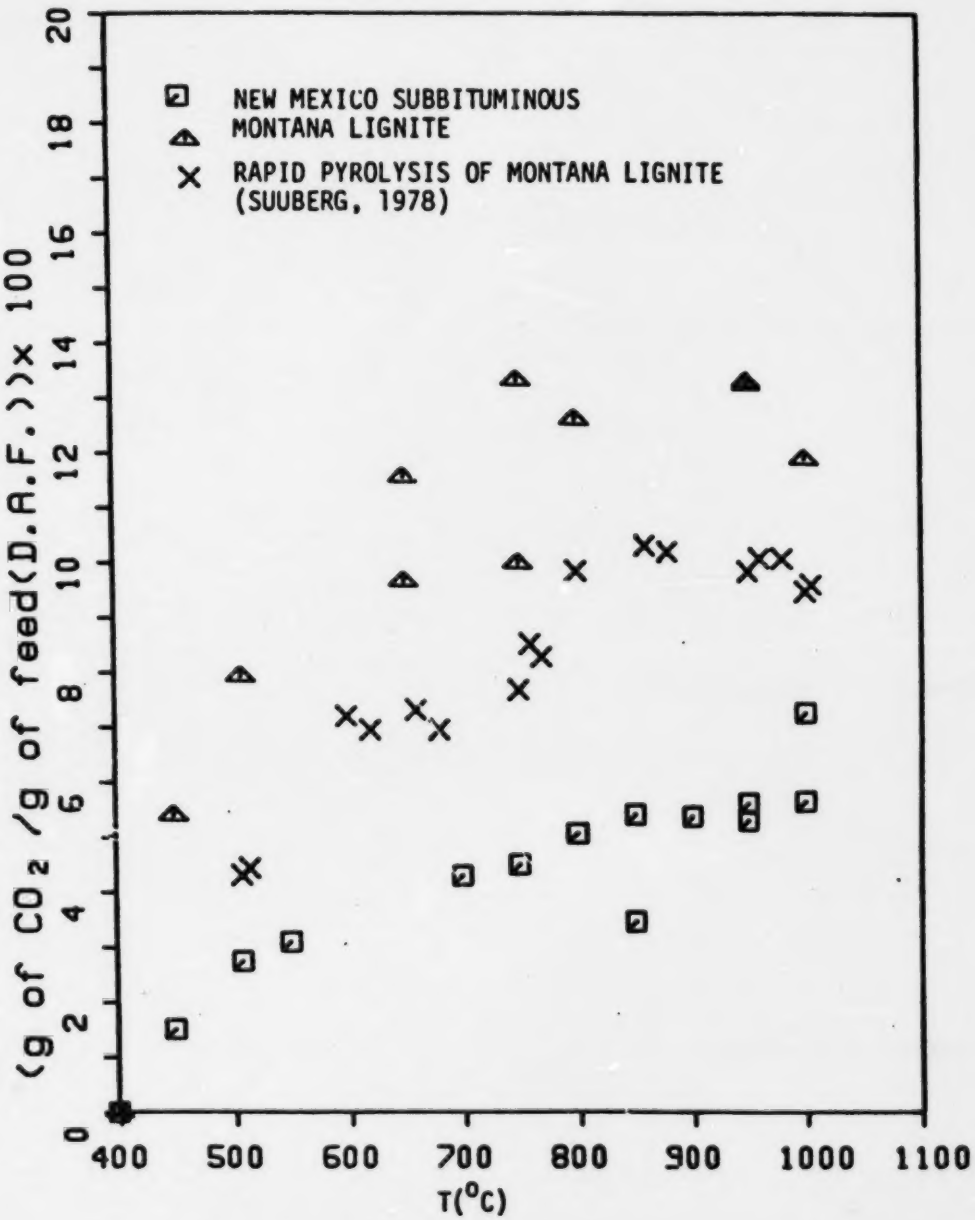

FIGURE 19 YIELDS OF CARBON DIOXIDE FROM THE SLOW AND RAPID PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

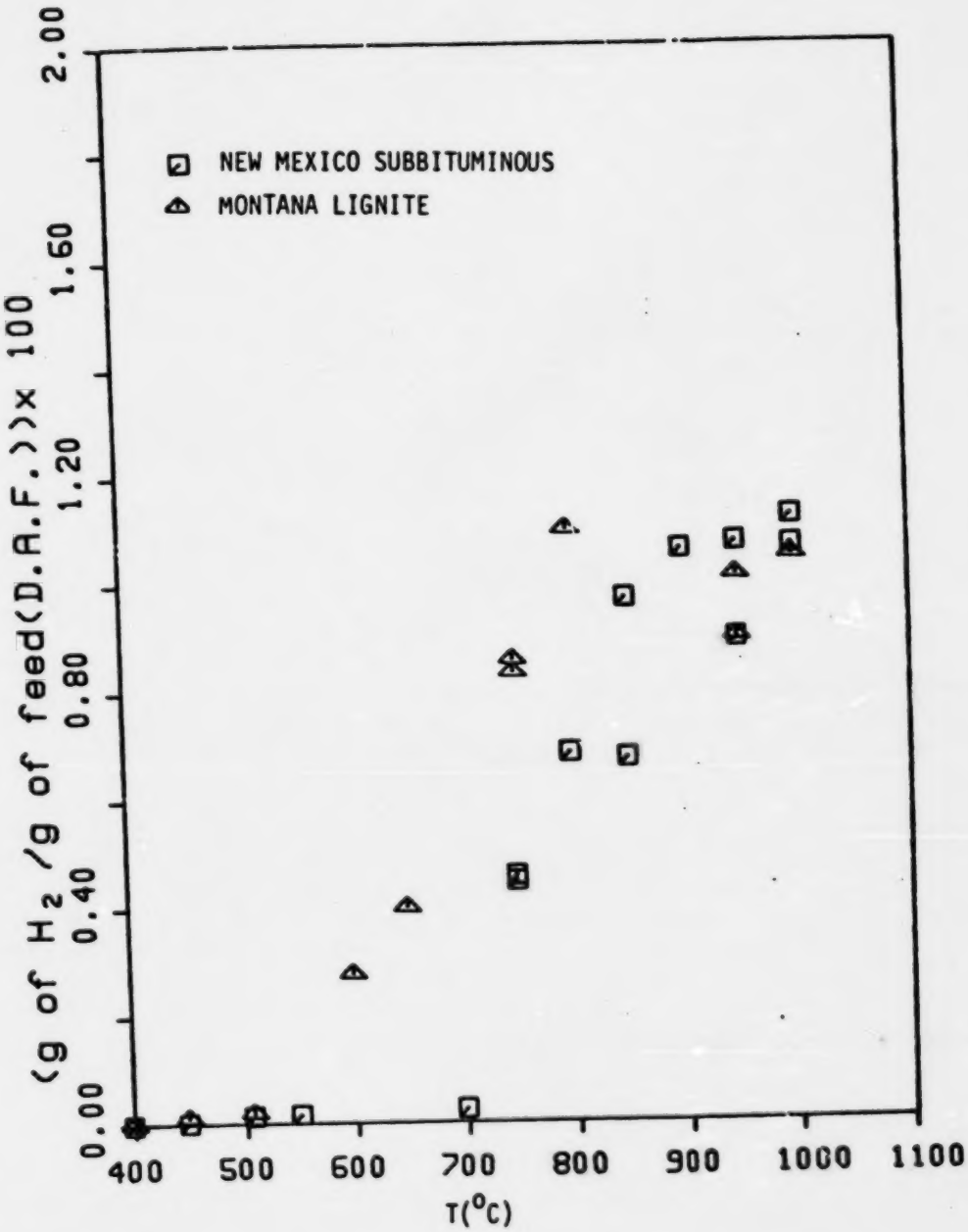

FIGURE 20 YIELDS OF HYDROGEN FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

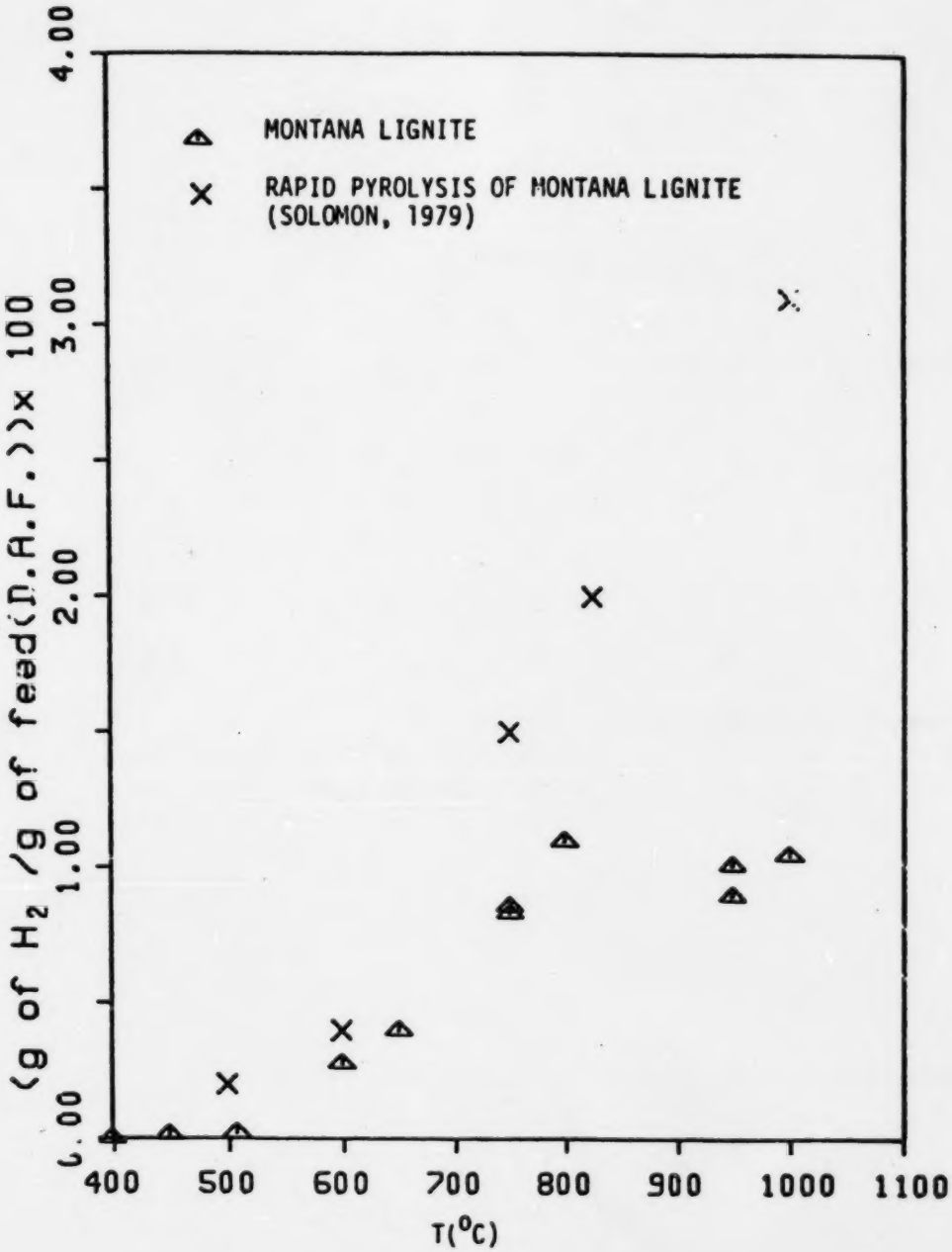

FIGURE 21 YIELDS OF HYDROGEN FROM THE SLOW AND RAPID PYROLYSIS OF LIGNITE

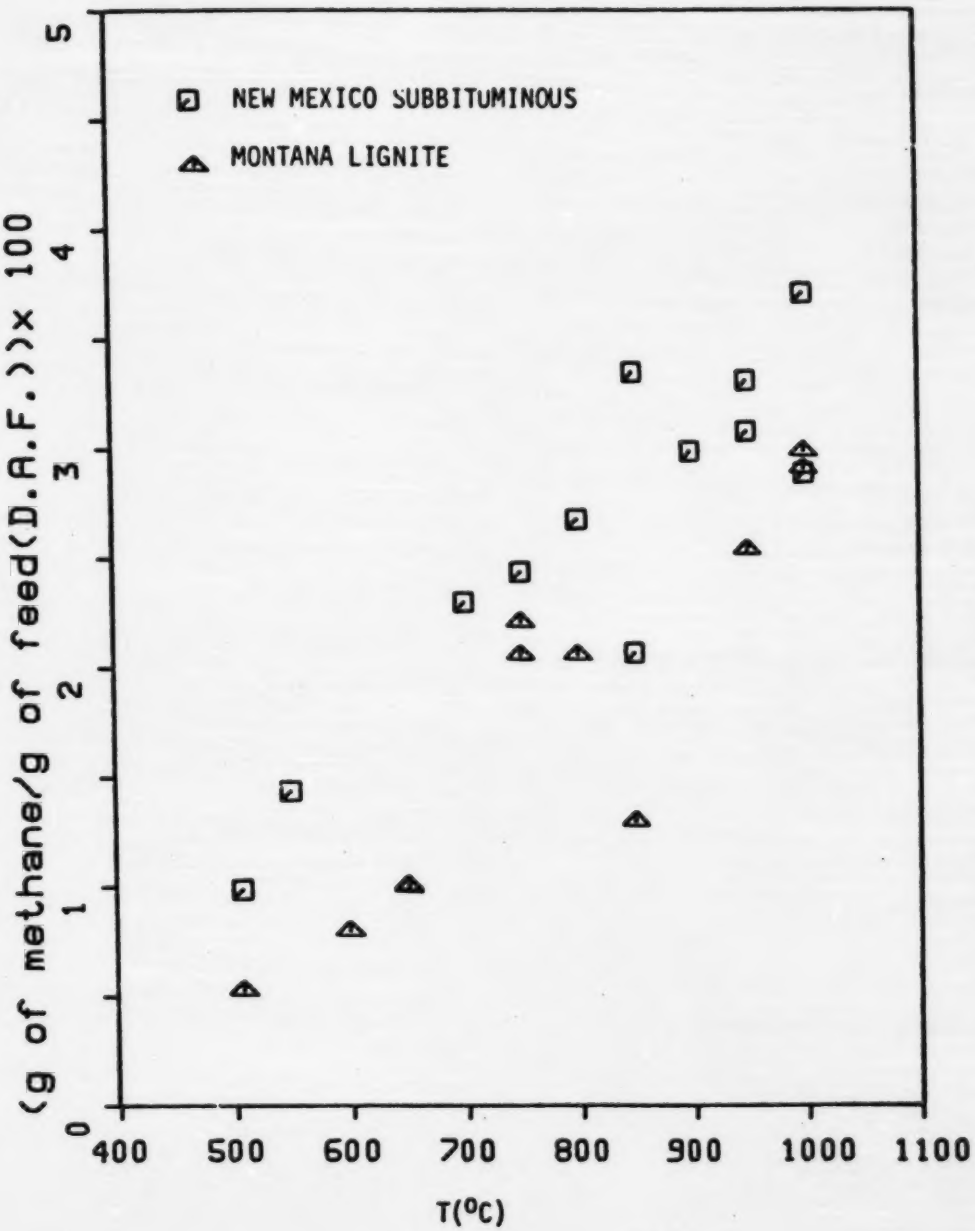

FIGURE 22 YIELDS OF METHANE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

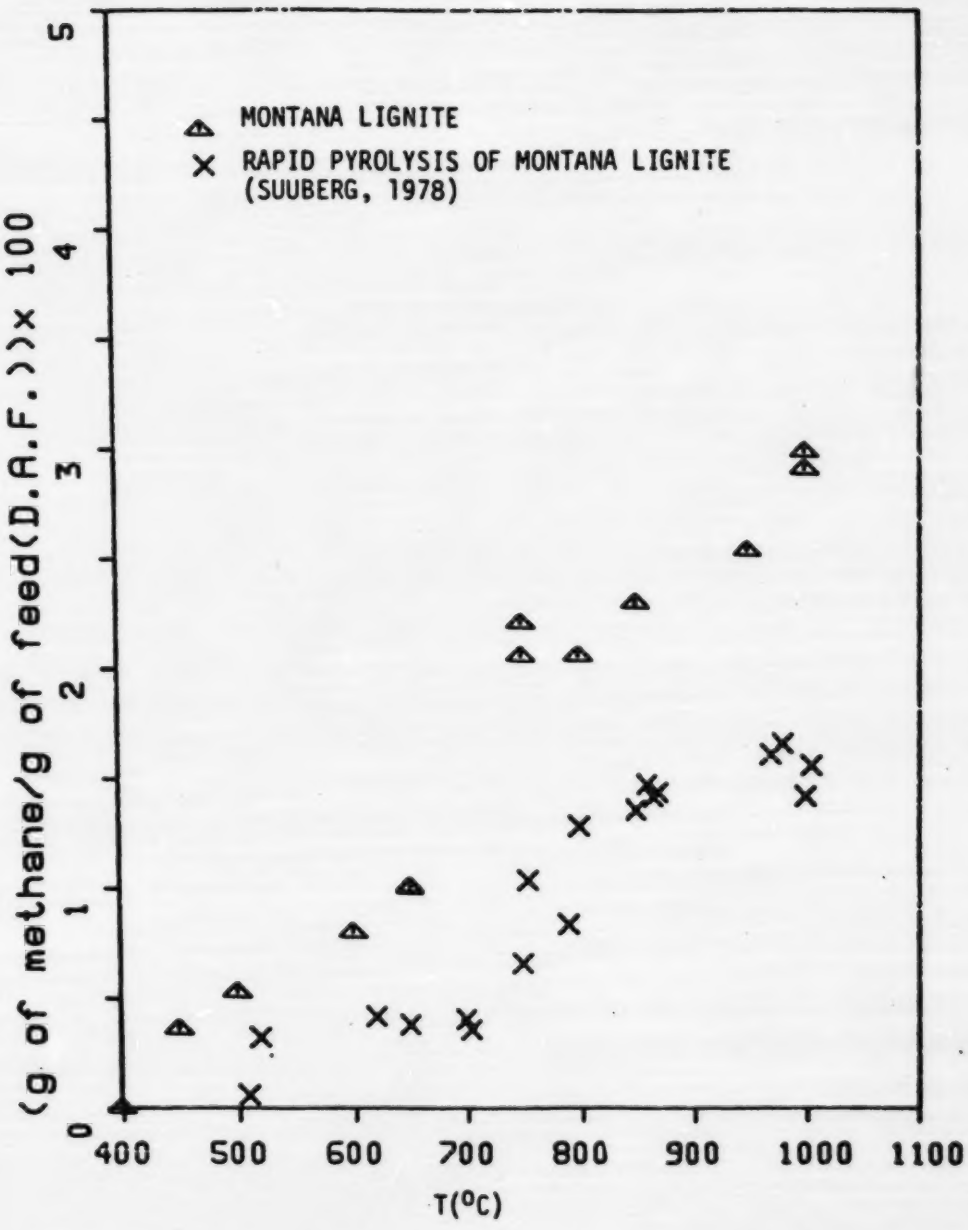

FIGURE 23 YIELDS OF METHANE FROM THE SLOW AND RAPID PYROLYSIS OF LIGNITE

Aliphatic Hydrocarbons. Yields of aliphatic hydrocarbons are shown in Figures 24 and 25. Methane was the predominant aliphatic hydrocarbon produced from the fluidized bed pyrolysis of subbituminous coal and lignite. According to Campbell and Stephens (1976), methane and other light hydrocarbons (ethane, ethylene, propane, propene, butane, and butene) are formed at low temperatures as the result of dealkylation. The major side groupings in coal in descending concentrations are methyl, ethyl, and propyl with small amounts of butyl. At higher temperatures (>600°C), methane is also produced from char autohydrogenation reactions (Fitzgerald and Van Krevelen, 1959).

Asymptotic yields for several low molecular weight aliphatic hydrocarbons are shown individually in Figures 26-30. The following observations emerge from an inspection of these figures.

1. The asymptotic yield of each aliphatic hydrocarbon species was greater for subbituminous coal than lignite;

2. Production of each alkene was greater than that of the corresponding alkane;

3. Ethylene yields increased with temperature for fluidized bed pyrolysis of subbituminous coal but decreased for lignite at temperatures greater than 900°C. Similar yields of ethylene from lignite (Suuberg et al., 1978) were produced by rapid pyrolysis.

4. Yields of all aliphatics larger than ethylene were maximized between 700 and 800°C. Further increases in temperature resulted in decreasing asymptotic yields.

Aromatic Hydrocarbons. The aromatic hydrocarbons measured include benzene, toluene, and xylene. Minor quantities of ethylbenzene were occasionally detected as well. Heavier aromatics could have been present, but they were below the discrimination and detection limits of the gas chromatograph.

At temperatures less than 700°C the yields of benzene, toluene, and xylene were similar for both subbituminous coal and lignite feedstocks. (See Figures 31 and 32.) The production of benzene increased dramatically at temperatures greater than 700°C. For both feedstocks, the yields of toluene and xylene at temperatures greater than 700°C showed marginal increases relative to the benzene yields. At 1000°C the yield of benzene was approximately ten times greater than that of xylene and three times greater than that of toluene. Data used to generate the curves for benzene, toluene, and xylene in Figures 29 and 30 are presented in Figures 33-35.

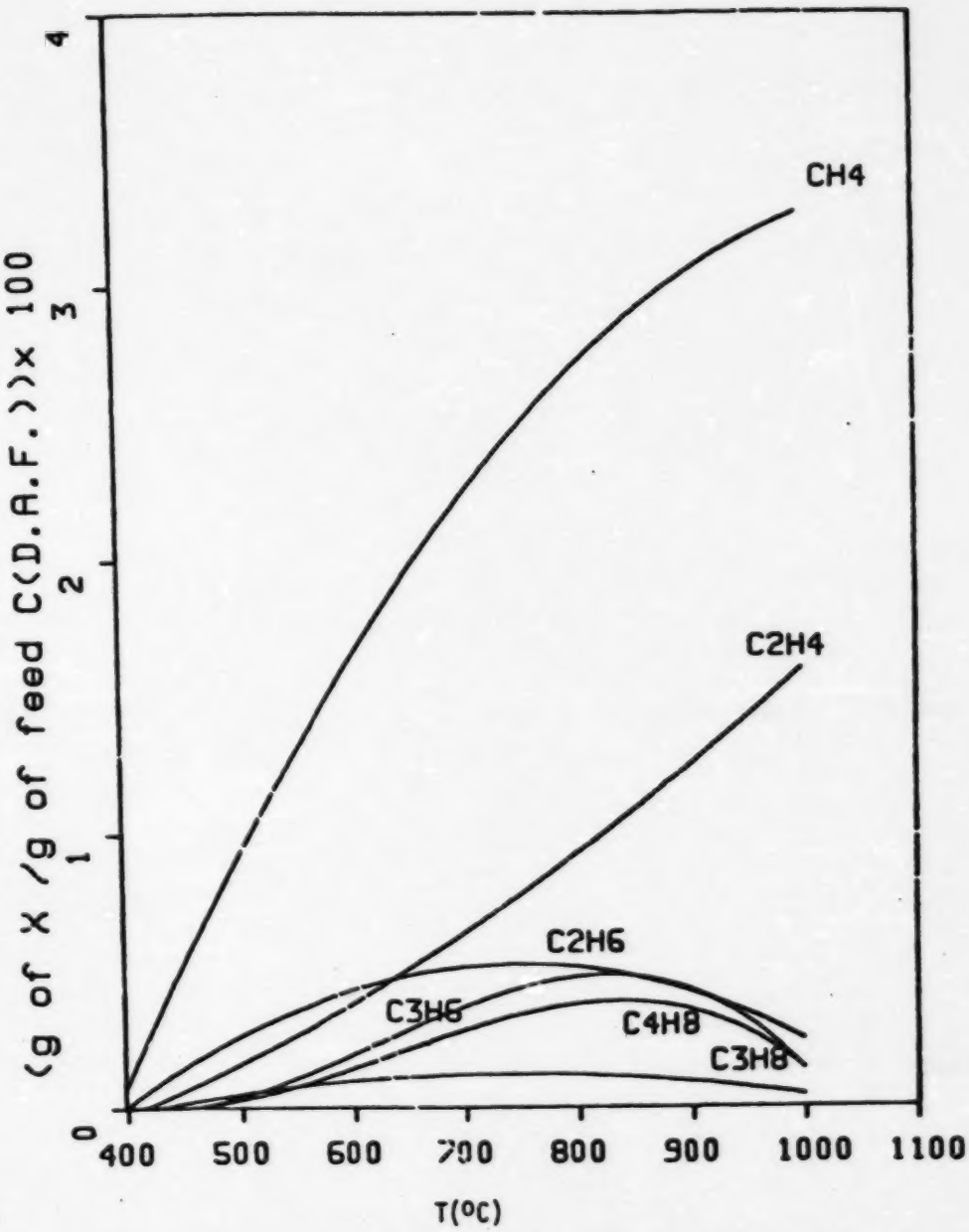

FIGURE 24 YIELDS OF ALIPHATIC HYDROCARBONS FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL

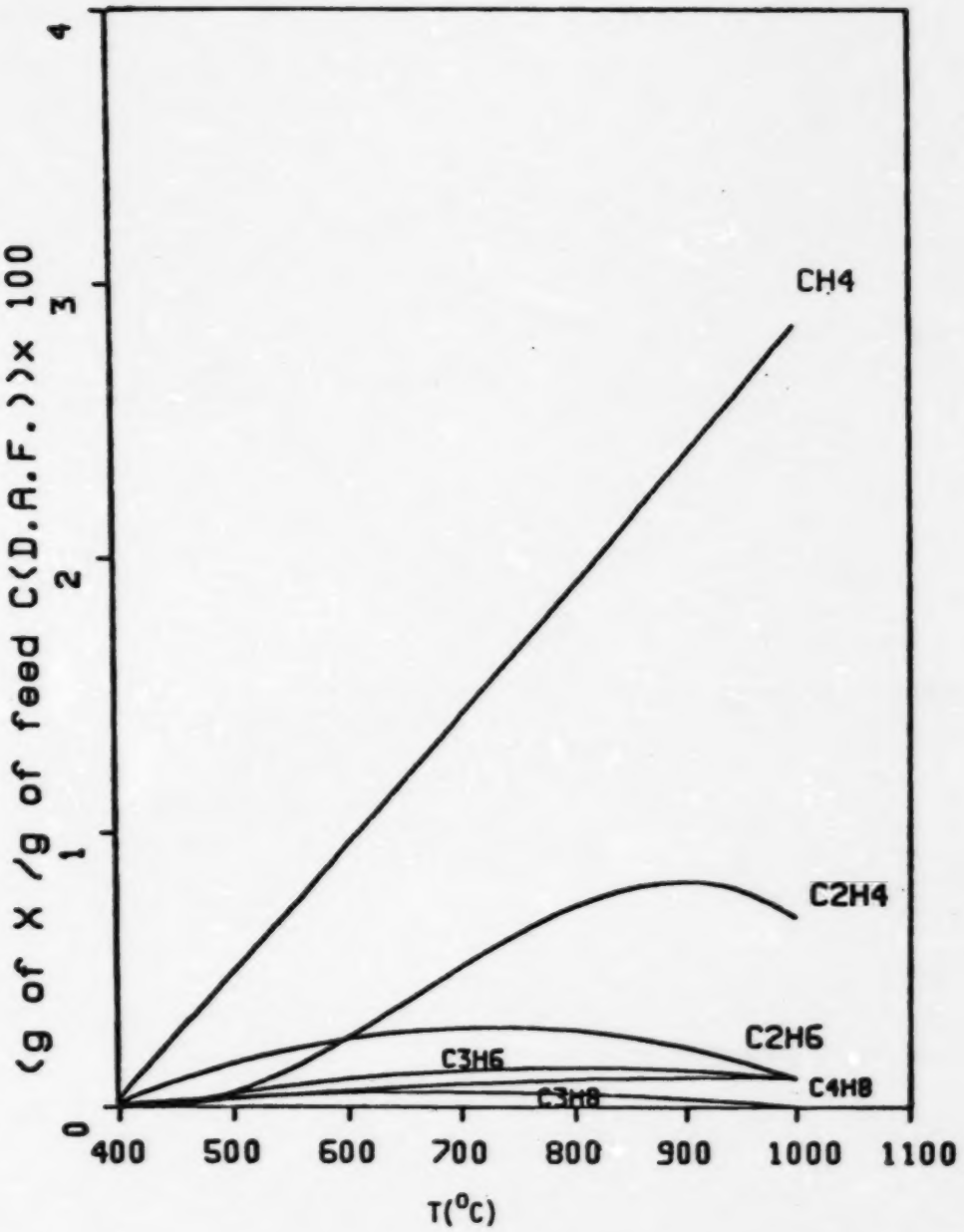

FIGURE 25 YIELDS OF ALIPHATIC HYDROCARBONS FROM THE SLOW PYROLYSIS OF LIGNITE

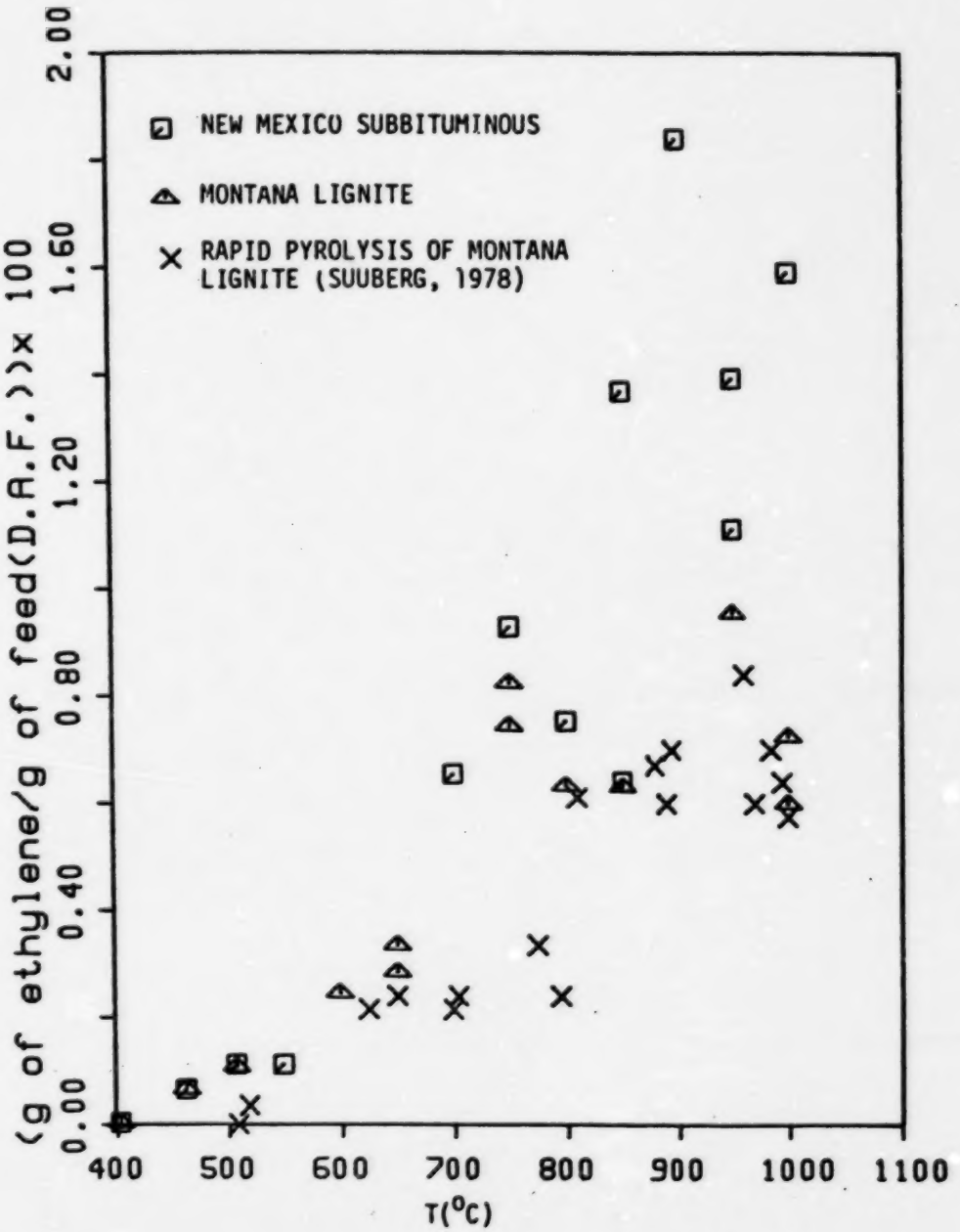

FIGURE 26 YIELDS OF ETHYLENE FROM THE SLOW AND RAPID PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

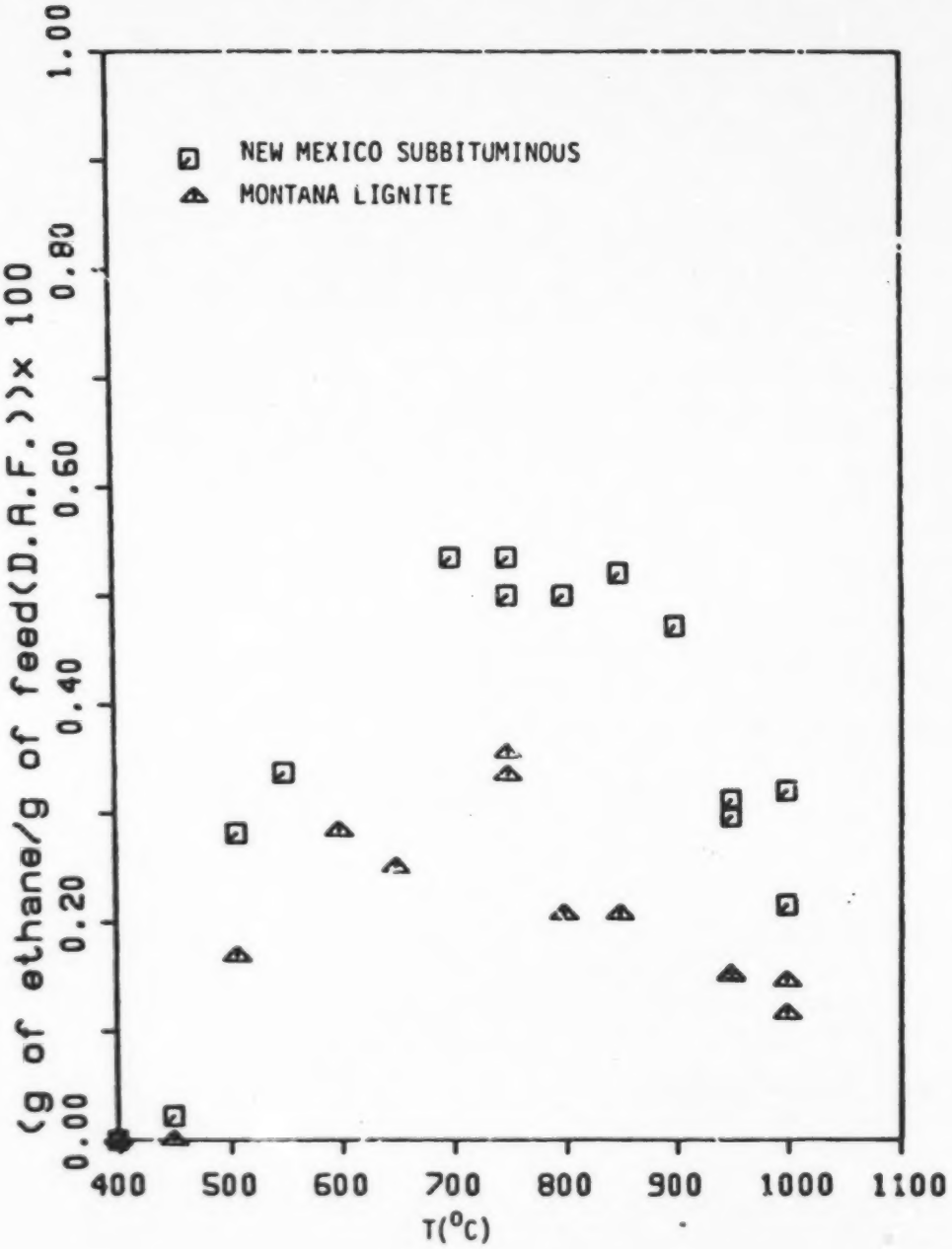

FIGURE 27 YIELDS OF ETHANE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

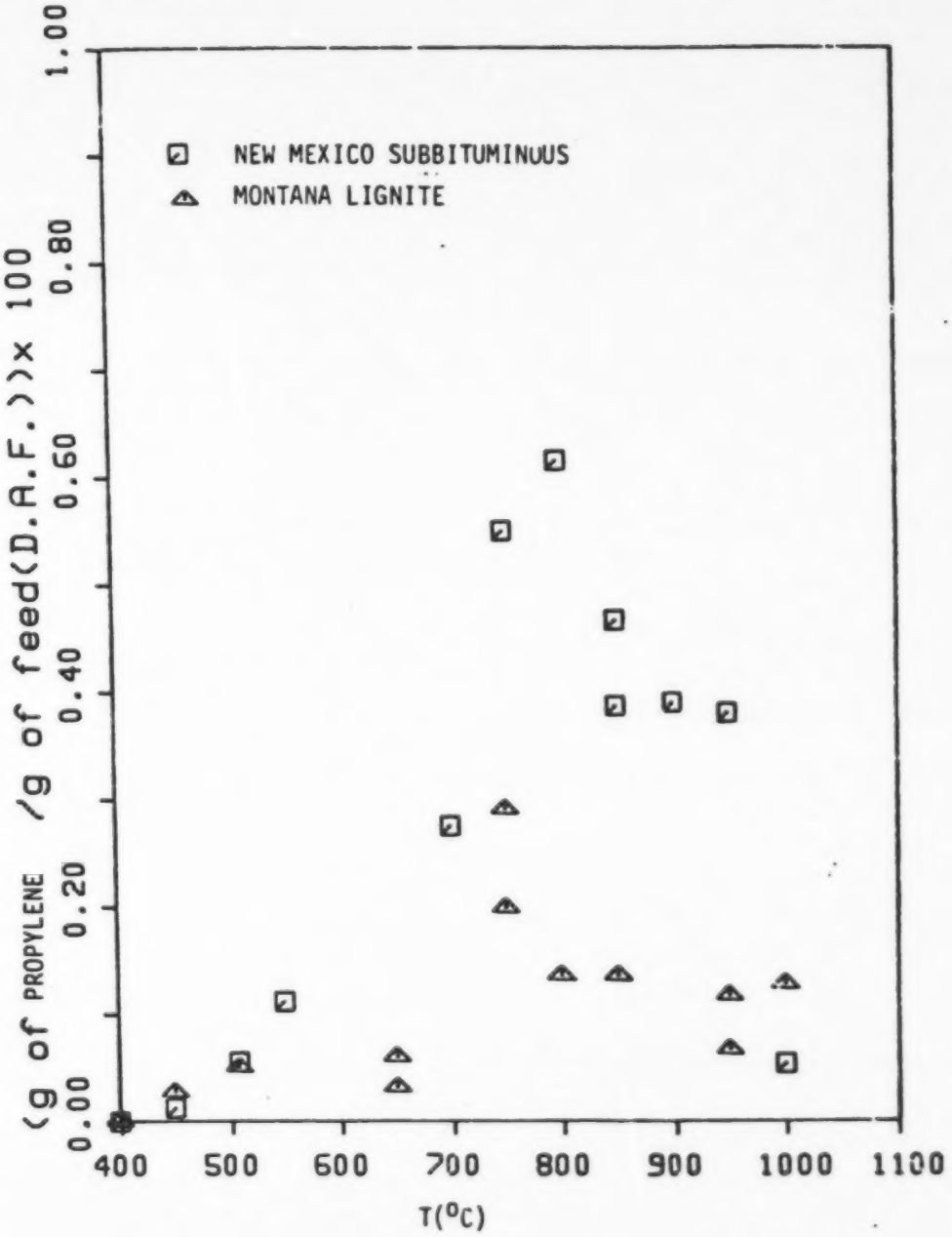

FIGURE 28 YIELDS OF PROPYLENE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

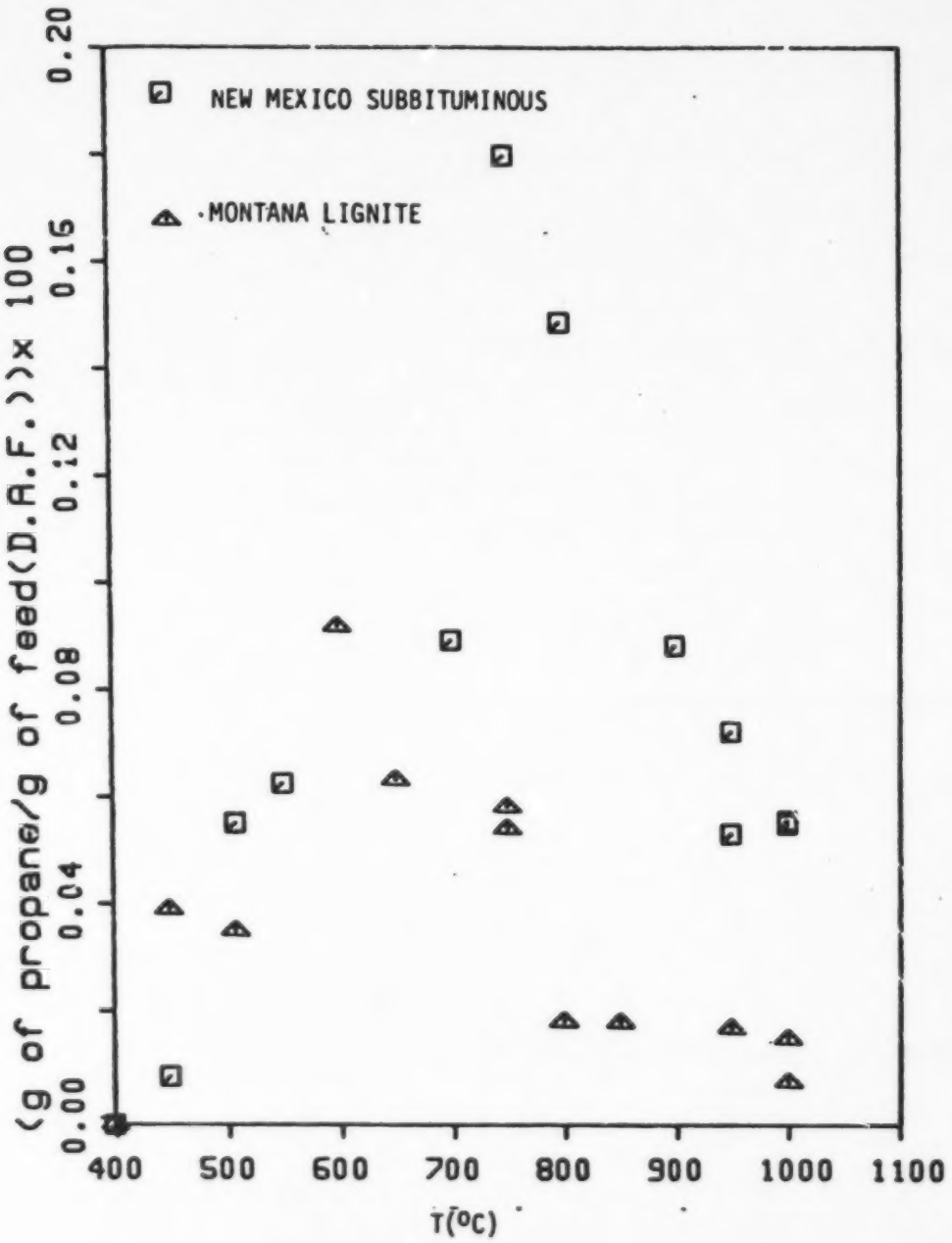

FIGURE 29 YIELDS OF PROPANE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

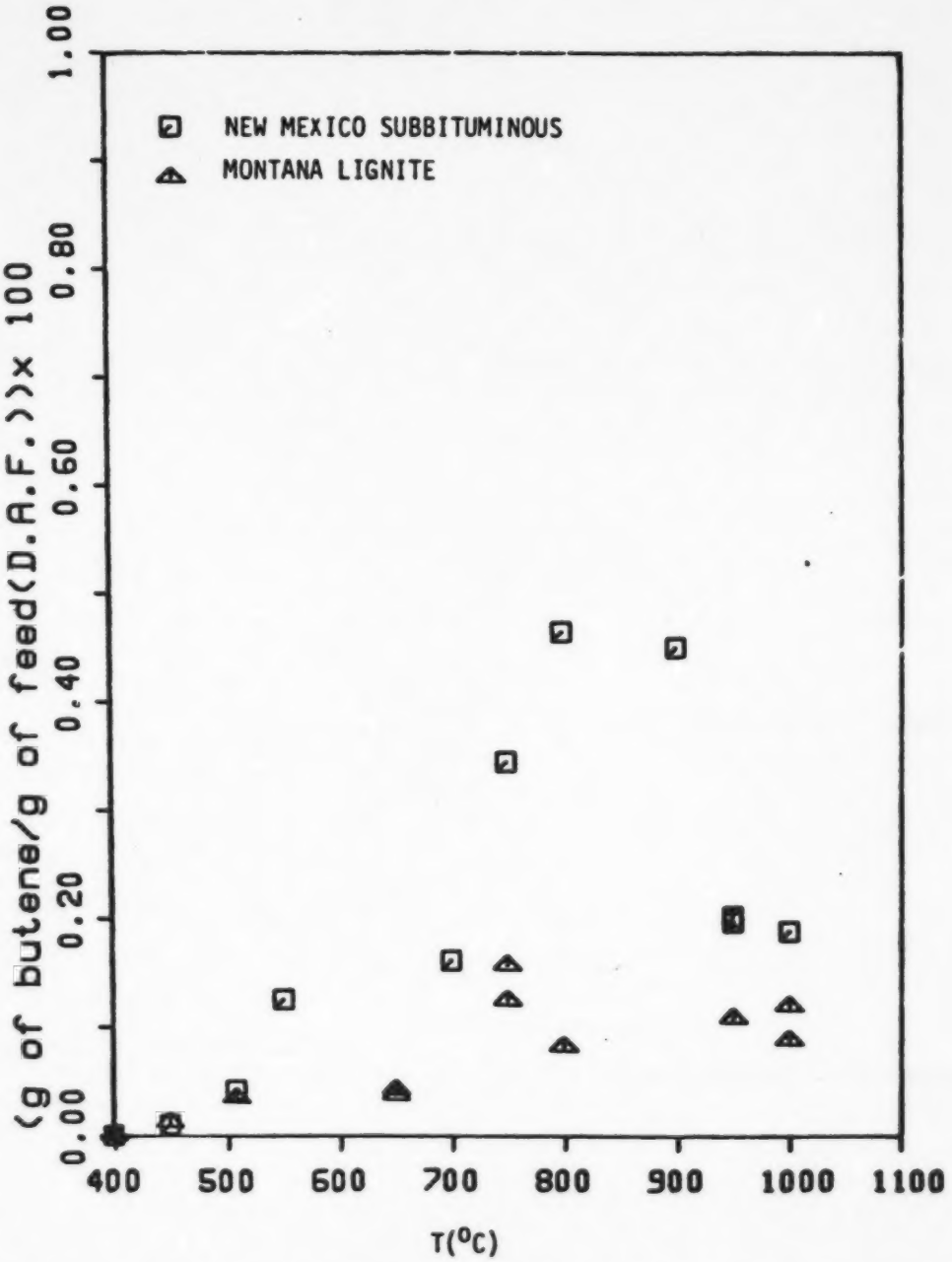

FIGURE 30 YIELDS OF BUTENE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

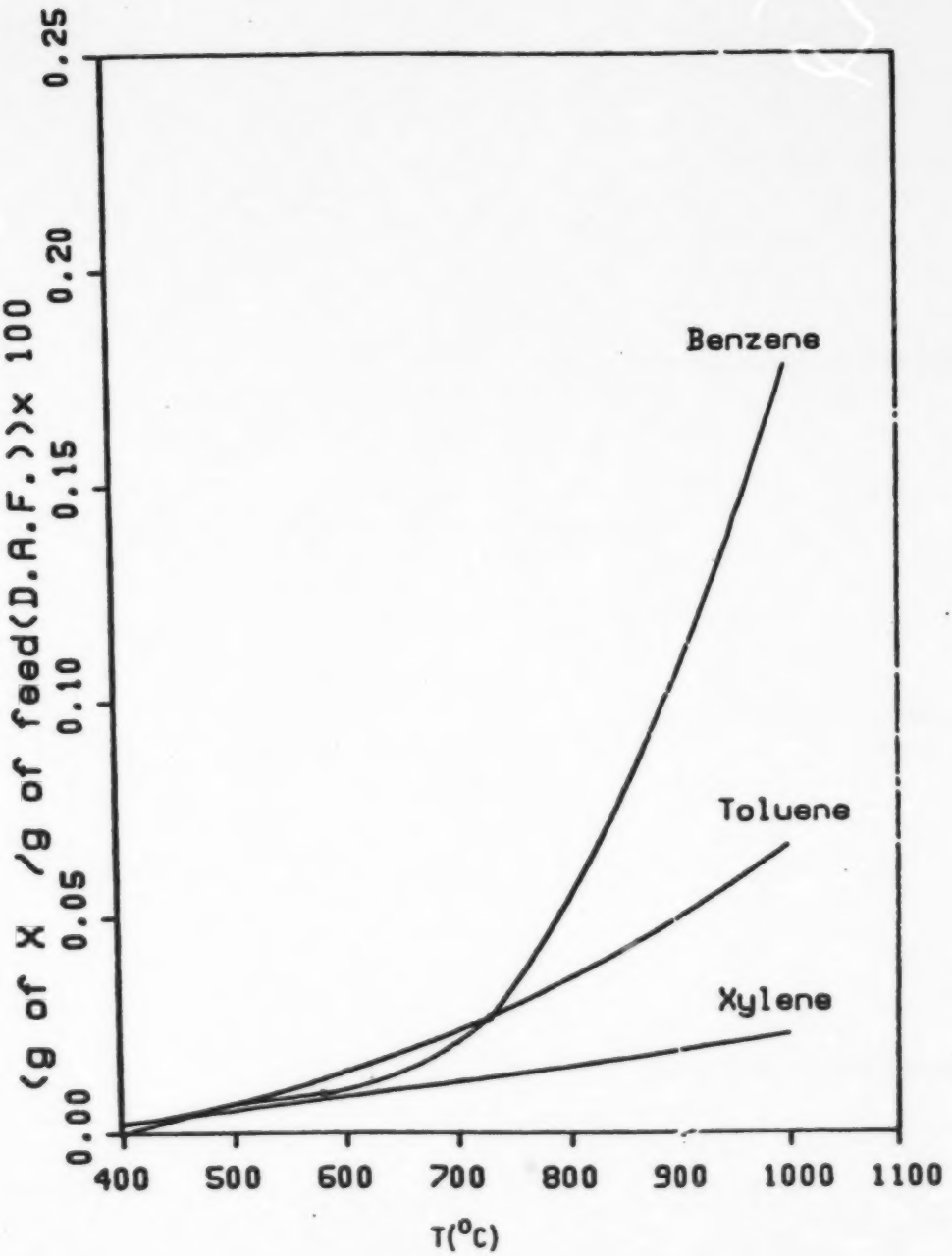

FIGURE 31 YIELDS OF AROMATIC HYDROCARBONS FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL

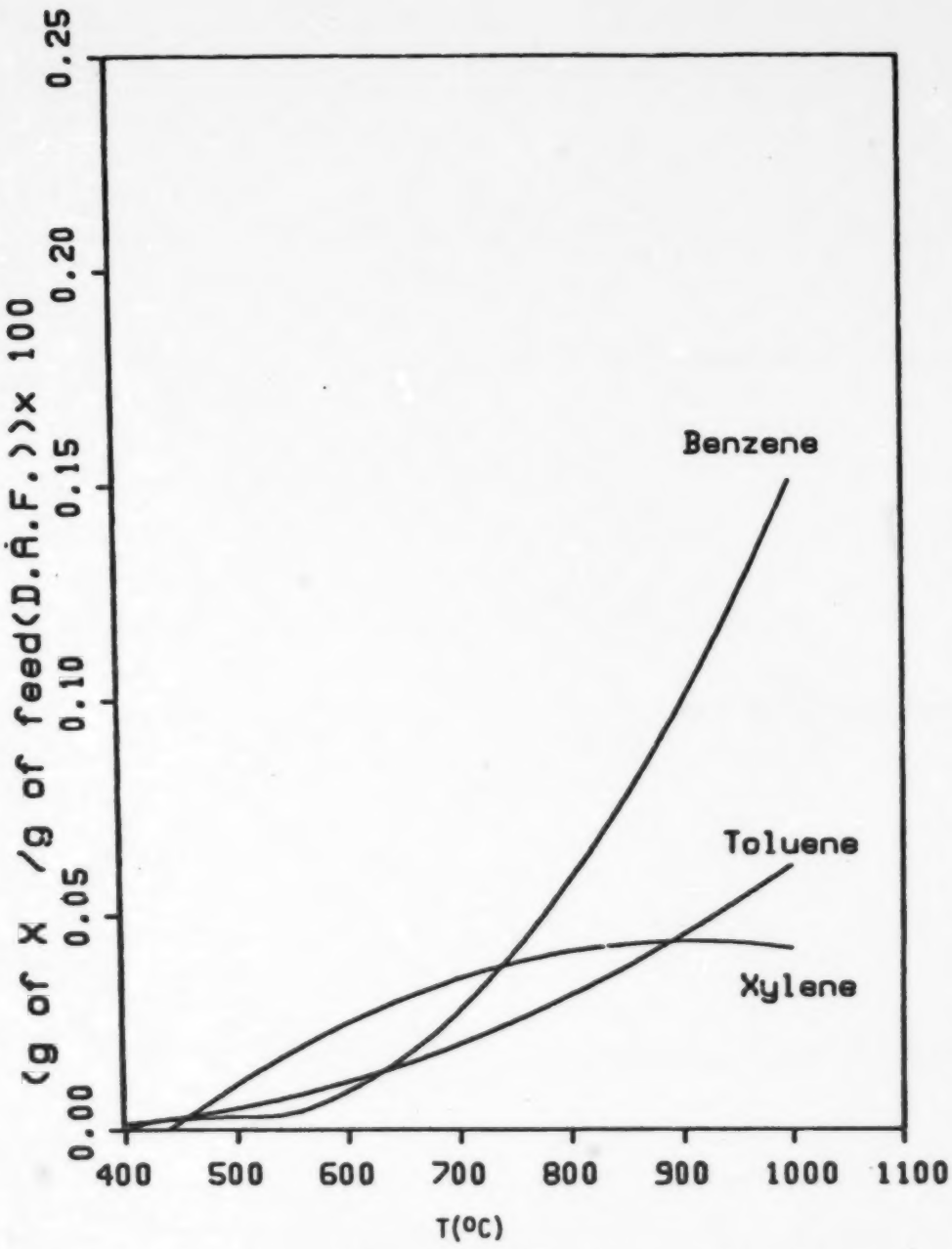

FIGURE 32 YIELDS OF AROMATIC HYDROCARBONS FROM THE SLOW PYROLYSIS OF LIGNITE

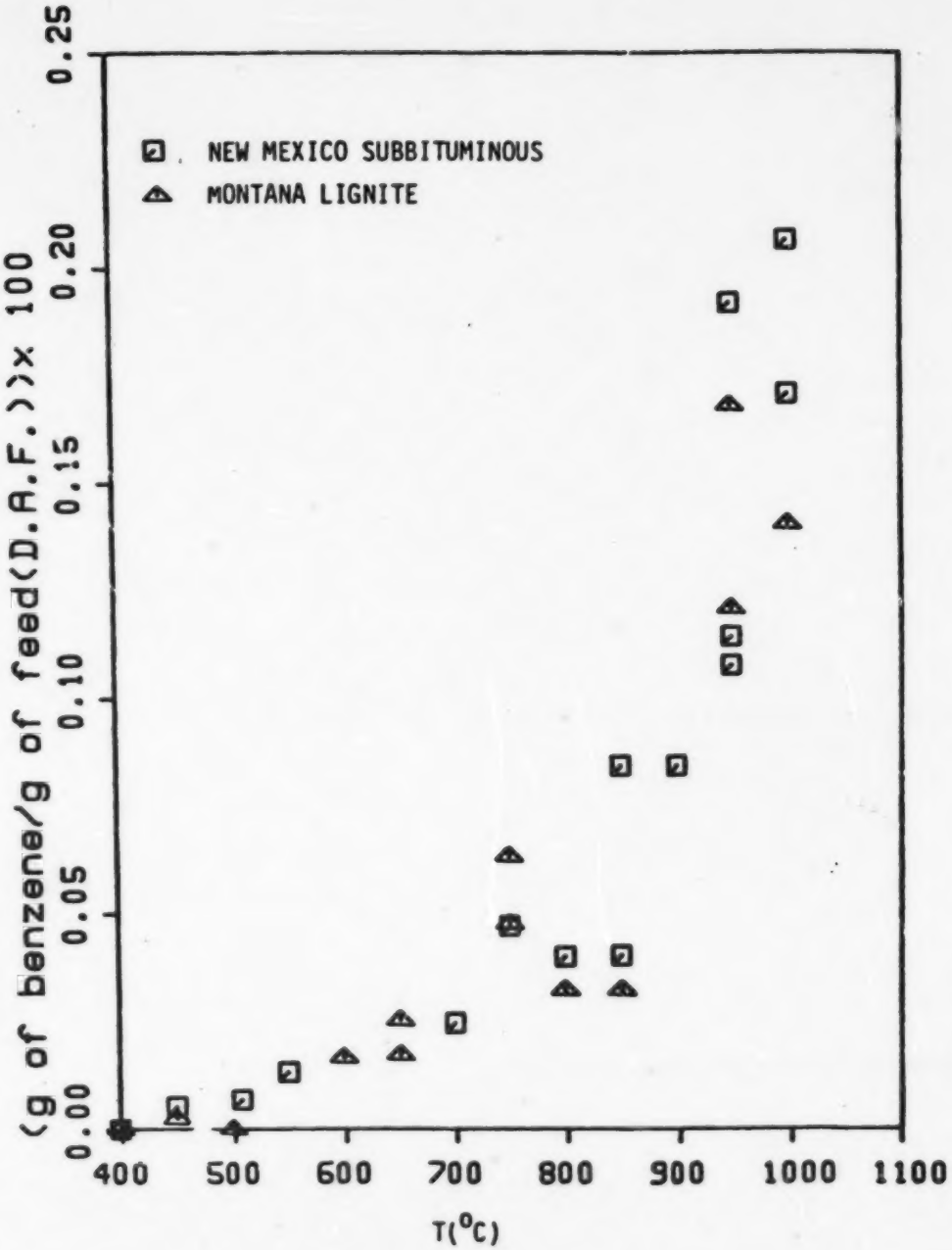

FIGURE 33 YIELDS OF BENZENE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

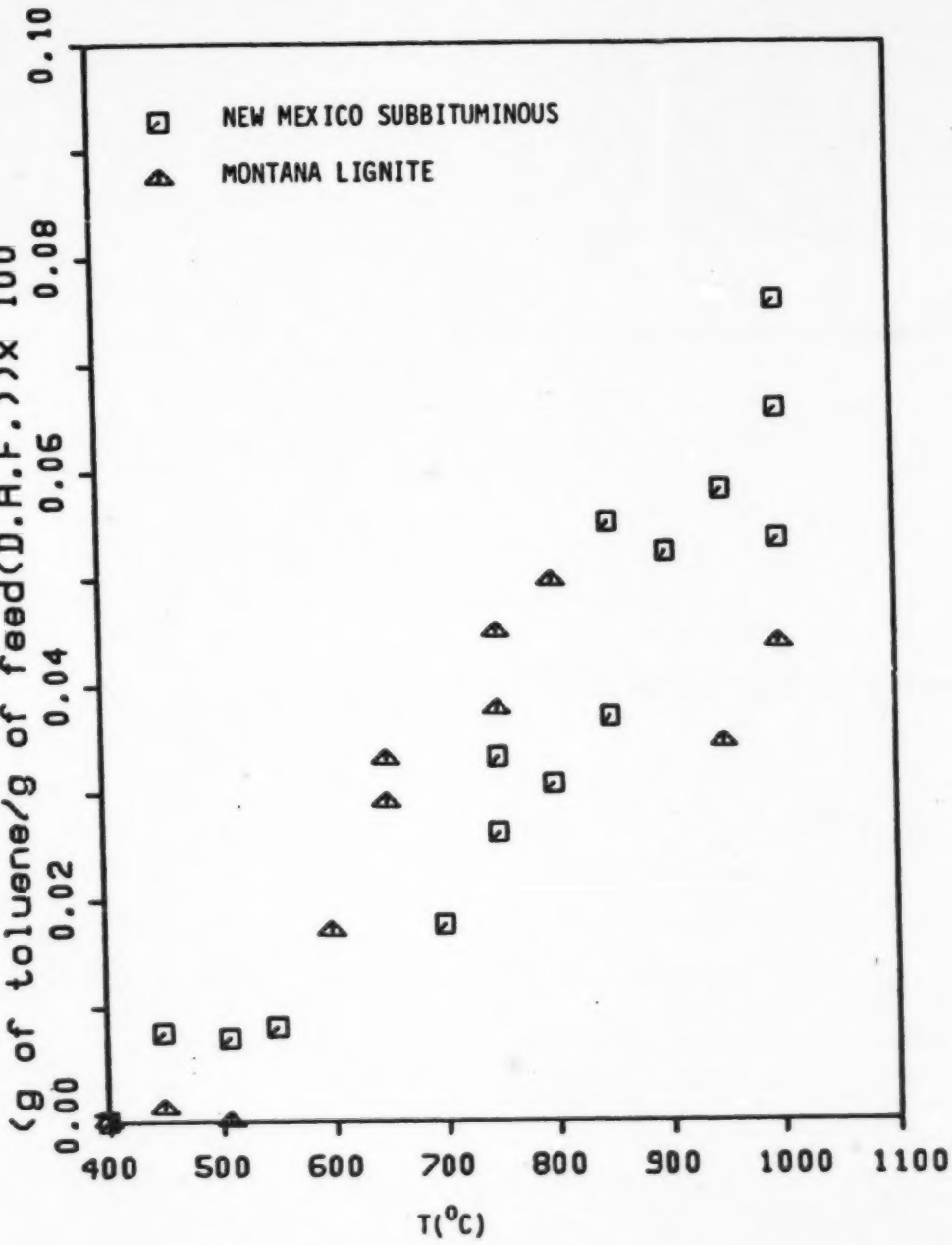

FIGURE 34 YIELDS OF TOLUENE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

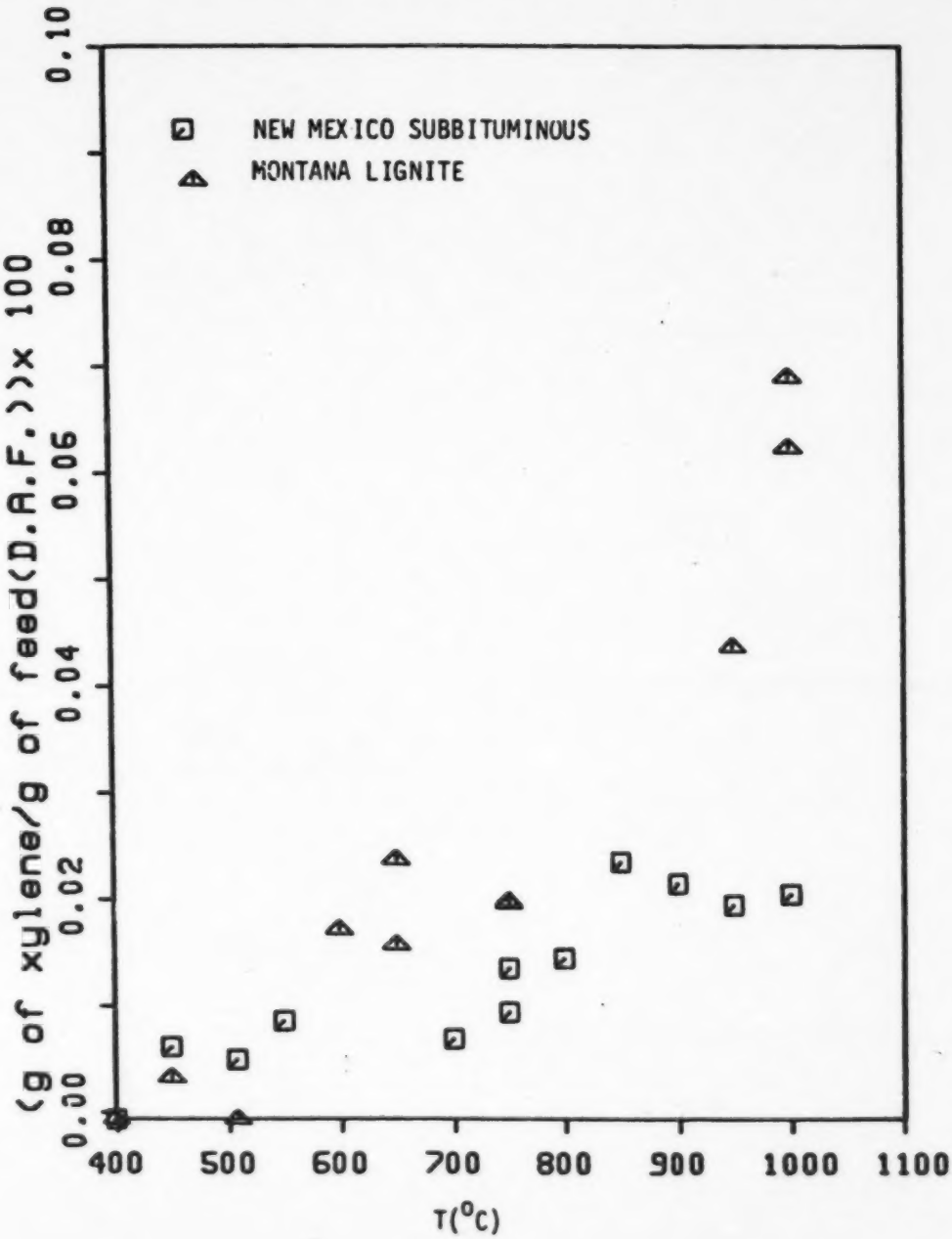

FIGURE 35 YIELDS OF XYLENE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

Sulfur Gas Species. Sulfur gas species found in the pyrolysis products include hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, and carbon disulfide. Yields of these species are shown in Figures 36-38.

Hydrogen sulfide was by far the predominant sulfur species formed. The decrease in the hydrogen sulfide emission rate observed for the slow pyrolysis of both coals at temperatures greater than 800°C (Figure 37) is consistent with the view of Attar(1978) that the volatilization of sulfur at these temperatures is limited by mass transfer. (See discussion on p. 36.)

Yields of carbonyl sulfide (Figure 40) were two to three times greater for the subbituminous coal than for the lignite. At temperatures greater than 700°C further COS production was marginal. Yields of thiophene (Figure 41) were similar for both feedstocks. Yields of methyl mercaptan (Figure 42) for both coals showed maxima at about 700°C.

Carbon disulfide was produced from the pyrolysis of subbituminous coal in both the fluidized bed and fixed-bed reactors at temperatures greater than 800°C. It was not produced in the fluidized bed pyrolysis of lignite. Conversely, ethyl mercaptan was produced in the fluidized bed pyrolysis of lignite but did not appear in the products of either the fixed-bed or fluidized bed pyrolysis of subbituminous coal.

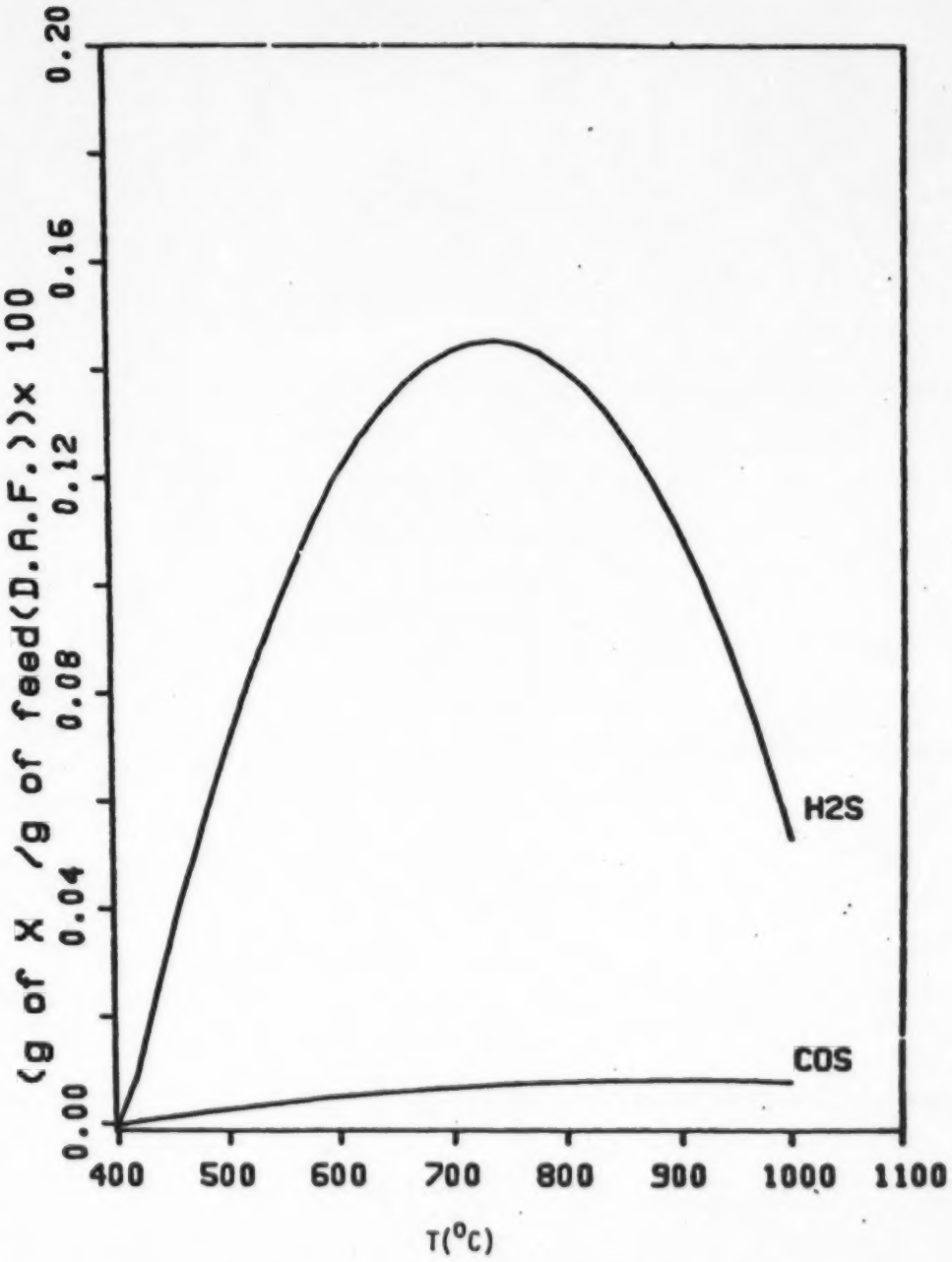

FIGURE 36 YIELDS OF H_2S AND COS FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL

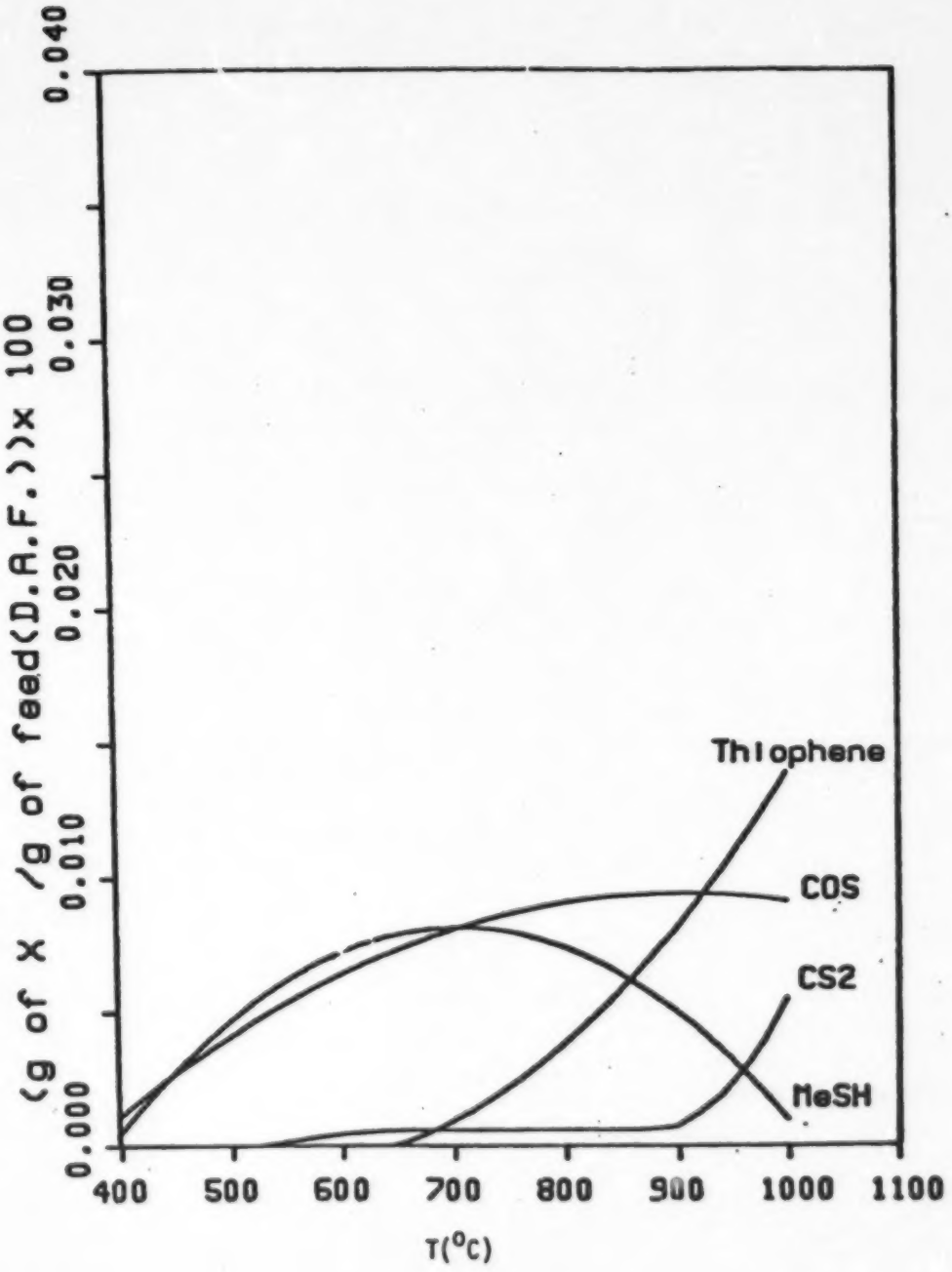

FIGURE 37 YIELDS OF SULFUR GASES OTHER THAN H_2S FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL

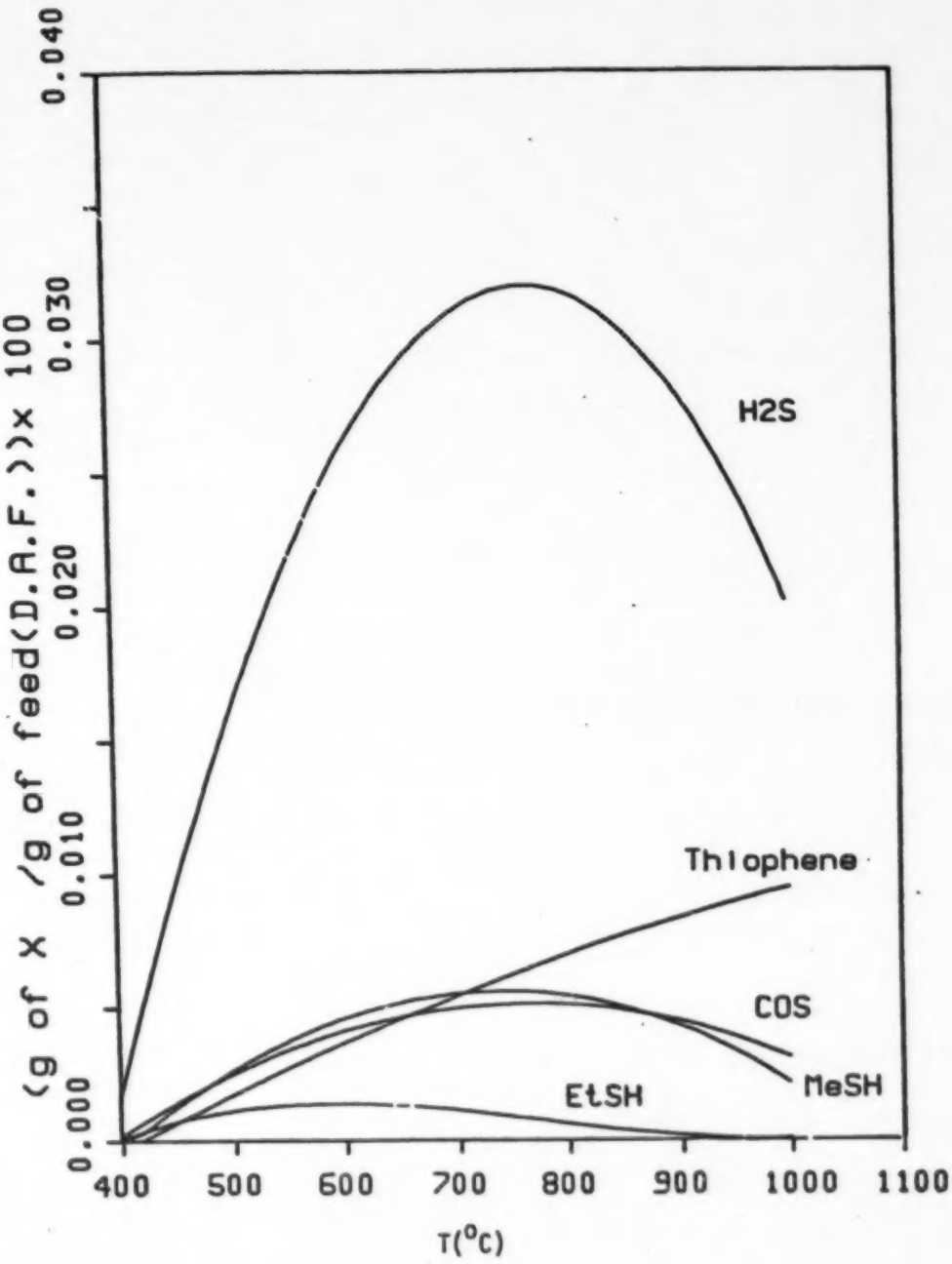

FIGURE 38 YIELDS OF SULFUR GASES FROM THE SLOW PYROLYSIS OF LIGNITE

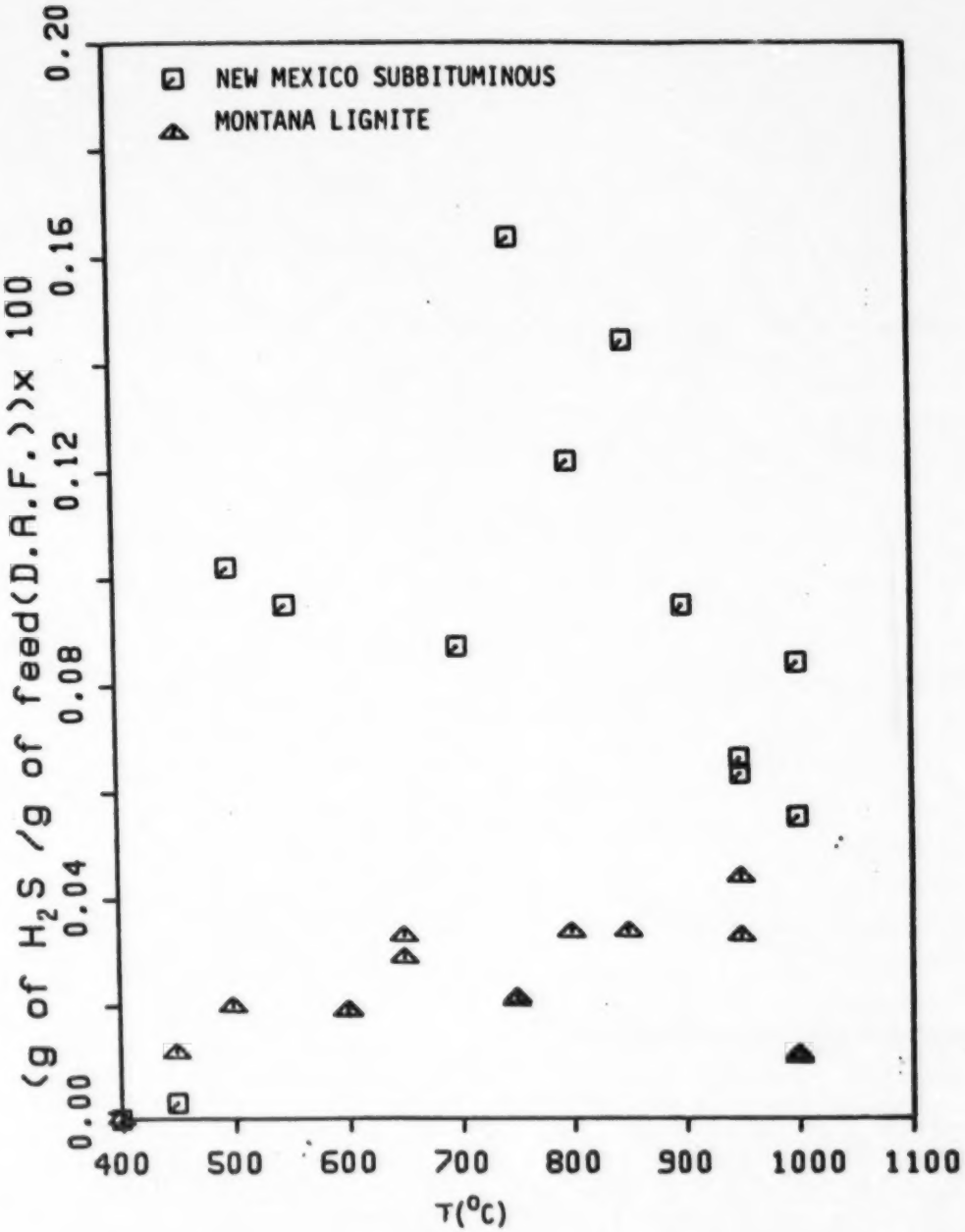

FIGURE 39 YIELDS OF HYDROGEN SULFIDE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

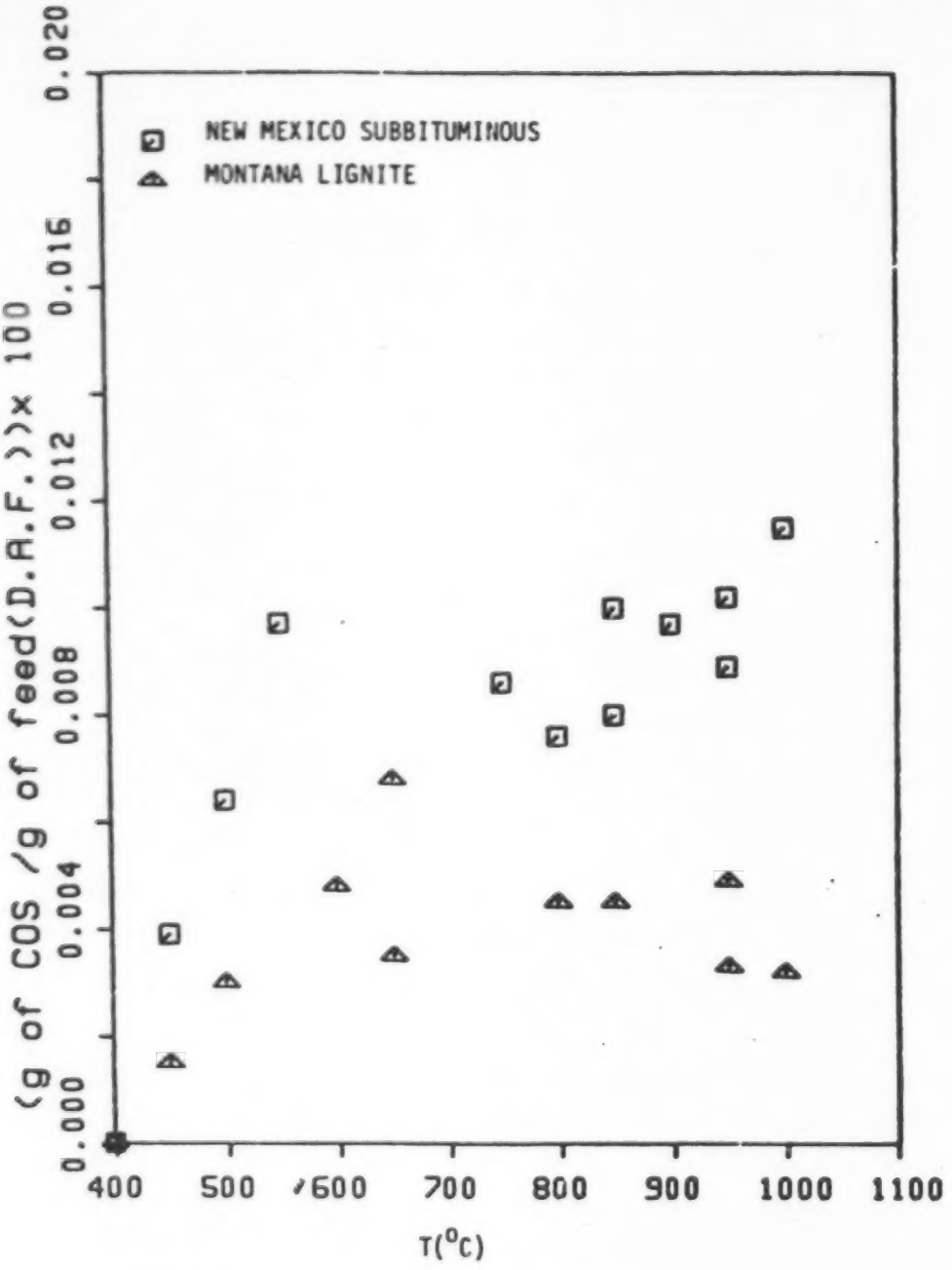

FIGURE 40 YIELDS OF CARBONYL SULFIDE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

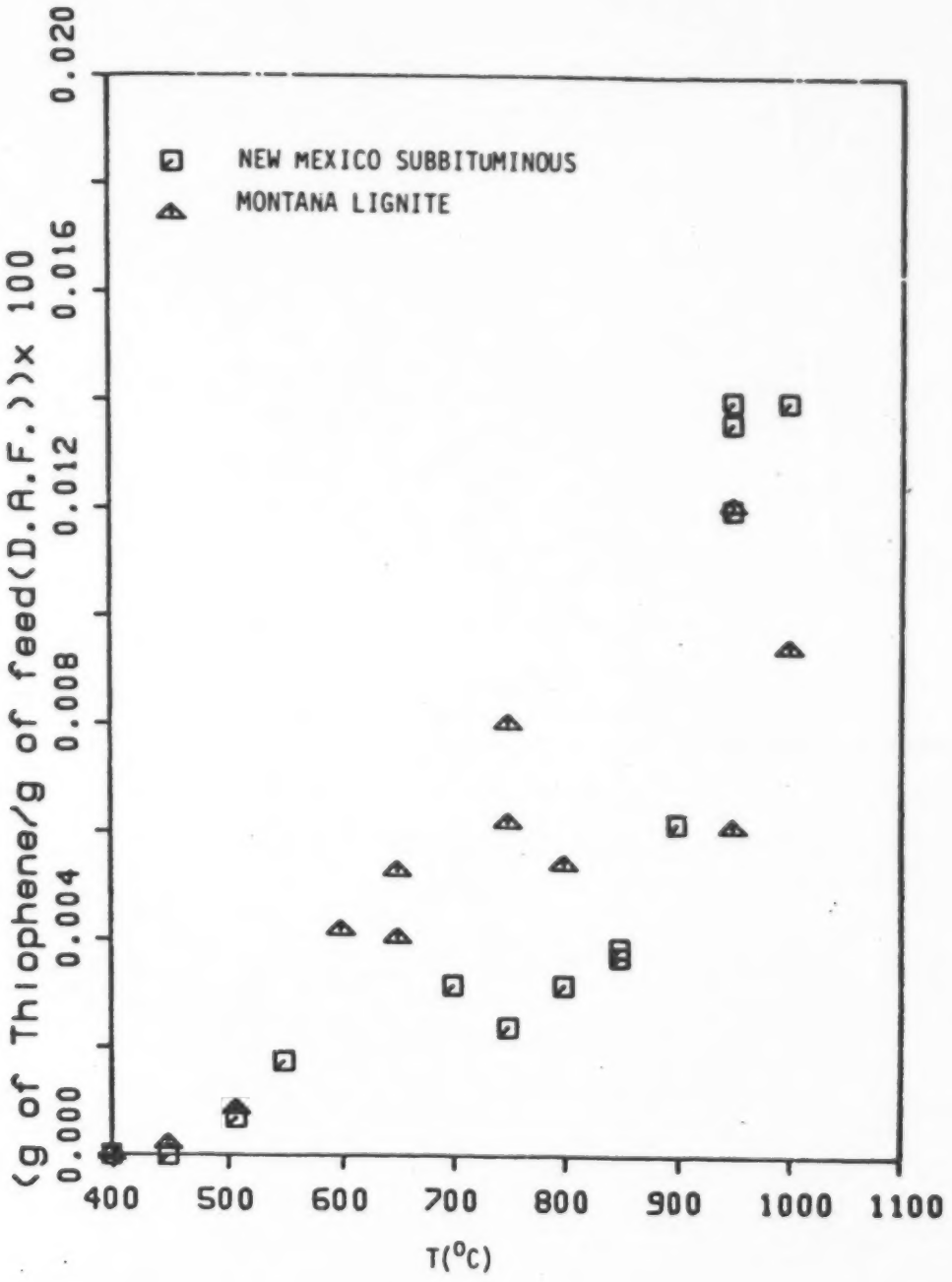

FIGURE 41 YIELDS OF THIOPHENE FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

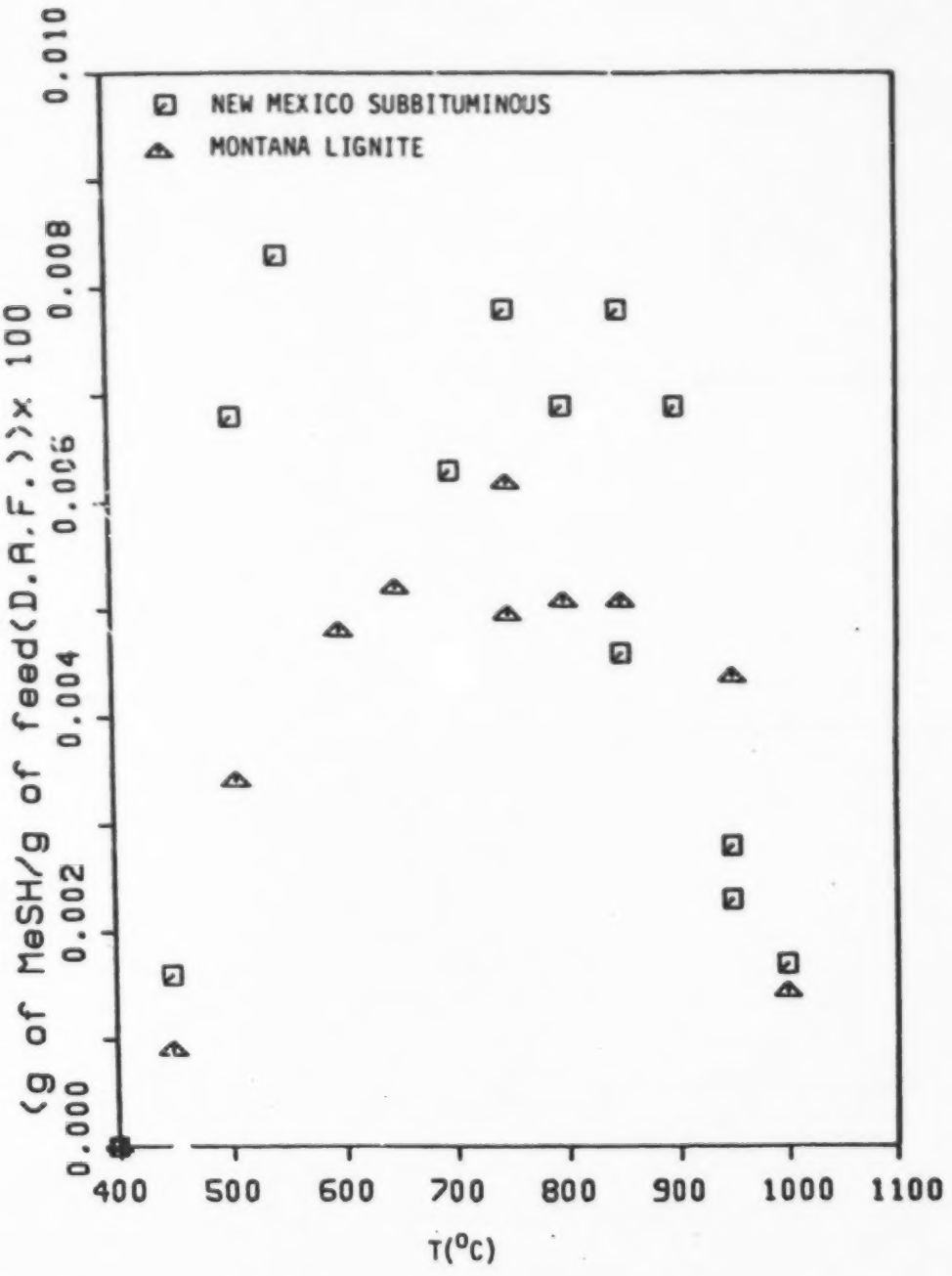

FIGURE 42 YIELDS OF METHYL MERCAPTAN FROM THE SLOW PYROLYSIS OF SUBBITUMINOUS COAL AND LIGNITE

QUALITY CONTROL EVALUATION REPORT

Replicate runs were performed for both reactors at all conditions studied. The fractional devolatilization and fractional emissions of major species generally agreed within 20% in replicate runs; fractional emissions of trace species showed a much broader degree of scatter, but generally agreed within 50%.

Mass balance closures provided the principal means of assessing the validity of the results. The closures were generally between 90% and 100% for the fluidized bed reactor, as shown in Tables 7 and 8. The material not accounted for is probably mostly tar and heavy organics which condensed on the reactor walls and in the lines. There is also a possibility that some condensed material revolatilized in the drying step that constituted part of the routine sample preparation procedure. In consequence, the reported tar-to-gas ratios could be 10-15% too low. However, the speciation of the evolved gas should not be affected.

The mass balance closures achieved with the fixed bed reactor were less satisfactory, on the order of 80-85%. Again, insufficient collection of tar and water undoubtedly accounts for most of the discrepancy. Design changes to improve the performance of this reactor could have been made, but were not once it was determined that the fluidized bed provided more reliable data. The conclusions derived in the study are based on the results obtained with the fluidized bed.

Replicate runs were performed in all chemical analyses, with as many runs being performed as necessary to achieve a standard deviation of 3% or less. The gas chromatographs were fully recalibrated using gas standards at no more than two week intervals, with spot checks being run every day to assure that no drift had occurred.

The measured fractional devolatilizations are consistent with results obtained in other published slow pyrolysis studies, as shown in Figure 9. This lends additional credence to the individual speciation results, which constitute the principal original contribution of this research.

SUMMARY AND CONCLUSIONS

The evolution of volatile matter was studied for a subbituminous coal pyrolyzed in a bench scale fixed bed reactor and for both a lignite and subbituminous coal pyrolyzed in a bench scale fluidized bed reactor. The pyrolysis products -- tar, water, char, and gases -- were separated and analyzed. Fixed gas, aliphatic hydrocarbon, aromatic hydrocarbon, and sulfur gas species were quantified by gas chromatography. Total mass and elemental balances were obtained.

All coals exhibited a dramatic increase in pyrolytic weight loss(d.a.f.) between 400 and 850°C. Further increase in temperature only produced marginal increase in weight loss(d.a.f.).

Plots of asymptotic(long-time) weight loss vs. temperature for the slow pyrolysis(<45°C/s) of five coals(Montana Lignite, Montana Savage Lignite, Montana Subbituminous, New Mexico Navajo Mine Subbituminous, and Pittsburgh Seam Bituminous) fell very close to a single curve over a temperature range of 400-1000°C. Asymptotic weight loss was correlated with temperature by the following equation:

$$\text{Weight Loss(d.a.f.)} = -49.06 + 0.20T(C) - 1.066\times10^{-4}T(C)^2$$

where T(C) = Temperature in degrees Celsius. Similar plots for the rapid pyrolysis(10^3 - 10^5°C/s) of three coals -- Montana Lignite, Montana Rosebud Subbituminous, and Pittsburgh Seam Bituminous -- based on published data also fell close to a single curve, which lies below the slow pyrolysis curve and approaches it at temperatures of about 900°C. Nonlinear regression was used to obtain the following formula for rapid pyrolysis:

$$\text{Weight Loss(d.a.f.)} = 165\exp[-0.000714\,T(C)] - 846\exp[-0.00310\,T(C)] + 1350\exp[-0.00587\,T(C)]$$

Extents of both hydrogen and oxygen volatilization increased with pyrolysis equilibrium temperature. Volatilization of both elements was 90% complete at 900°C in the fluidized bed for both feedstocks. Carbon was volatilized at temperatures ranging from 400°C to 800°C to a maximum extent of about 35%. Increases in temperature above 800°C did not increase carbon volatilization for either feedstock.

Sulfur volatilization increased with temperature in the fixed bed pyrolysis of subbituminous coal. In the fluidized bed pyrolysis of both lignite and subbituminous coal the sulfur volatilization was maximized between 700 and 900°C. These results are consistent with a postulate that sulfur release in this temperature range is governed by the available internal surface area of the char and the intraparticle porosity.

The rates of formation of tar and water in the fluidized bed pyrolysis of the two coals, lignite and subbituminous coal, differed significantly. Tar production for the subbituminous coal approached 20% by weight of the feed(d.a.f.) between 500 and 700°C whereas the production of tar from lignite pyrolysis was erratic and never more than 3-5%. In contrast, water production was much greater for lignite than subbituminous coal.

The tar yield from the fluidized bed pyrolysis of subbituminous coal decreased at temperatures greater than 700°C. The drop in tar production yielded an increase in the gas fraction of the volatiles.

The production of water from the fluidized bed pyrolysis of lignite dropped between 900 and 1000°C. At the same temperatures carbon monoxide and methane productions increased with no discernable change in hydrogen production. A possible reaction path would involve a steam-char reaction followed by char autohydrogenation.

In the fixed bed pyrolysis of subbituminous coal, gas yields of hydrogen, carbon monoxide, carbon dioxide, methane, benzene, thiophene, and carbon disulfide increased with temperature. Yields of toluene, xylene, C2-C4 aliphatic hydrocarbons, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan were maximized at temperatures between 700 and 900°C. In the fluidized bed pyrolysis of both lignite and subbituminous coal, gas yields of hydrogen, CO, methane, ethylene, benzene, toluene, xylene, and thiophene increased with temperature, while the yields of carbon dioxide, pyrolytic water, ethane, C3-C4 aliphatic hydrocarbons, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan were maximized at temperatures between 700 and 900°C.

Carbon disulfide was produced from the pyrolysis of subbituminous coal in both the fluidized bed and fixed bed reactors at temperatures greater than 800°C. It was not produced in the fluidized bed pyrolysis of lignite. Conversely, ethyl mercaptan was produced in the fluidized bed pyrolysis of lignite but did not appear in the products of either the fixed bed pyrolysis or fluidized bed pyrolysis of subbituminous coal. Yields of ethyl mercaptan were lower than yields of methyl mercaptan.

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